Organic acidity characterisation of AMD in the Section Six pit of Mt Tom Price Mine, Pilbara, Western Australia.

A thesis submitted in partial fulfilment of the requirements for the

Degree of Master of Engineering Geology

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by J.C. Hedley

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This thesis is dedicated

to the memory of my Grandma

Daisy Hedley

19th May 1929 - 1st June 2012

An inspiration, through her hard work, generosity and dedication

Abstract

Temporal analyses of physical, geochemical and biological characteristics were used to define the acidity inconsistency issue identified in the Section Six (SSIX) pit of Mt Tom Price Mine, in the Pilbara region of Western Australia. The SSIX pit is used for on site storage of acidic mining water, before transfer to the on site Acid Water Treatment Plant for neutralisation. This study was initiated due to a 2007 investigation into the SSIX pit, which identified an acidity inconsistency between the calculated acidity (determined by metal ion concentrations; 45 mg/L as $CaCO_3$) and the total acidity (determined by acidity titration; 280 mg/L as $CaCO_3$). Based on this finding, it was hypothesised that the laboratory confirmed SSIX algal presence (in green coloured pit water) was potentially producing a weak/organic acidity unaccounted for in the calculated acidity.

Archived geochemical raw data for the SSIX pit water and its surrounding inputs (from nearly a decade of environmental monitoring) were used in a temporal analysis. This analysis produced a trend of increased major ions in solution during seasons/periods of high rainfall. This was related to archived aerial photos of the SSIX pit, which display typical (green) algal presence during dry seasons/periods when major ions in solution are lowest (a potential lower metal phytotoxicity).

A 2012 investigation into the SSIX pit determined an absence of algae, despite indication from green pit water colouration. From this, a new question was considered "what observations and measurements differ between water sampled in 2007 and 2012 that could explain either the absence of algae, or, any continued presence of acidity inconsistency".

The phytoplankton absence in 2012 was attributed to increased concentrations of major ions, causing phytotoxicity to phytoplankton growth, along with a decreased influence of phytoplankton input from source waters to the SSIX pit. These observations were opposite to the previous findings from 2007.

Three pit water colour categories were determined, to decipher between the opaque green water colour witnessed during the 2007 algal presence, the translucent green water colour witnessed during the 2012 algal absence (attributed to copper and

aluminium green precipitates) and the brown pit water colour during periods of high total dissolved solids (attributed to iron red precipitate and thus further metal phytotoxicity). These categories can continue to be used as an indicator for algal presence or absence before laboratory confirmation.

Despite algal absence in 2012, titrations were still undertaken to characterise acid species in solution. Organic acidity was not observed, most likely due to the absence of algae. A large acidity inconsistency was also not observed, which tends to support the hypothesis that algal presence in 2007 provided cause (potential organic acidity) for acidity inconsistency. However inconclusive, it is also suggested that organic acidity is not the sole cause of acidity inconsistency, but rather an influential key player during dry seasons. Literature provides evidence that acidity inconsistencies can also occur from non-organic sources such as the presence of alkalinity in a water sample, metal sequestration, or errors in lab methods and reporting.

Future research into the SSIX pit should be undertaken during a time of algal growth to further determine potential organic acidity production.

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Abbreviations

AMD – Acid and Metalliferous Drainage
ANC – Acid Neutralising Capacity
ANZECC - Australia and New Zealand Environment Conservation Council
AWDG – Australian Drinking Water Guidelines
AWTP – Acid Water Treatment Plant
BOD – Biological Oxygen Demand
COD – Chemical Oxygen Demand
EC – Conductivity
LOR – Limit Of Reporting
MCS – Mt McRae Black Shale
NAF – Non-Acid Forming
SEP – South East Prongs
SSIX – Section Six
STR – Southern Ridge discharge
TDS – Total Dissolved Solids
TOC – Total Organic Carbon
TSS – Total Suspended Solids

Acknowledgments

Firstly, a big thank-you goes to RTIO for providing me with this thesis opportunity. Rosalind Green, thank-you for listening to my academic interests and allowing me to choose the most suited project topic to further educate my multidisciplinary interests. I am so grateful for your endless assistance and all the opportunities you have given me throughout working together.

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To my parents, Mike and Carolyn, for continuing to support my direction of study and never ending help with questions I have, no matter what hour of the day. Thank-you also goes to my sister, Francie, for supplying endless virtual hugs over Skype.

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1 Introduction and Background

1.1 Project background

Dewatering and depressurisation of groundwater in an open-pit mining operation is crucial to managing slope stability and progressing pit development. During this process, overburden and ore material become exposed to the atmosphere, which leads to oxidation of sulphide bearing minerals. In the absence of neutralising material, this results in the formation of acidic conditions that cause reduction in drainage water pH. Potentially toxic heavy metals are also released to the environment during this sulphide oxidation process (Buller, 2011). The acidic water can adversely impact the surrounding biosphere through degradation of water quality. Fortunately, such effects can be minimised by collecting the acid drainage in a storage pit and neutralised through the addition of alkaline reagents such as lime ($Ca(OH)_2$) or carbonate mineral ($CaCO_3$), or both.

Iron Ore mining operations at Mt Tom Price Mine, owned and operated by Rio Tinto Iron Ore and located in the Pilbara region of Western Australia, produce acidic drainage. At Mt Tom Price Mine, acidic mining water is stored in the Section Six (SSIX) pit before it is transferred to the acid water treatment plant (AWTP) and ultimately returned for mine use.

The use of the SSIX pit for water storage and treatment began after excessive rainfall during Cyclone Monty in 2004 caused an accumulation of surface water at Mt Tom Price mine, particularly in the South East Prongs (SEP) pit. The Mount McRae Black Shale, an overburden unit, at the bottom of the SEP pit contains sulphide minerals, predominantly pyrite (FeS_2). This shale caused the SEP surface water to become acidic; producing an environmental risk (Green, 2012; Hedley and Dogramaci, 2010). Thereafter, surface water, and water from dewatering and depressurisation bores in SEP pit, was transferred by active pumping to the SSIX pit (Gallagher, 2012).

The resulting water influx and other factors, has facilitated seasonal algal blooms in the now flooded SSIX pit. However, algal blooms typically occur in environments of nutrient enrichment and near neutral pH (only a minority of plants are able to grow at a pH below about 4.5; Begon et al., 2005); as opposed to the unusual algal bloom present in the acidic environment of the SSIX pit.

A 2007 investigation and analysis of the SSIX algal blooms indicates that the species present are of the phylum cyanobacteria and chlorophyceae (Brown, 2007). The chlorophyceae has been detected in concentrations as high as 392,040 cells/mL, while the cyanobacteria is known to occur at concentrations as high as 616 cells/mL (Brown, 2007).

Interestingly, the 2007 investigation also showed that the SSIX water exhibits an acidity inconsistency, with a high total titratable acidity despite having low concentrations of metals (Brown, 2007). The total titratable acidity in the SSIX pit water has been measured at 280 mg/L $CaCO_3$, whereas the acidity based on the metal concentrations and pH (calculated acidity) is 45 mg/L $CaCO_3$ (Brown. 2007). Such low pH, strong acid, aqueous environments are usually caused by the hydrolysis of metal ions to metal hydroxides, a process that releases hydrogen ions (H^+). However, given the general absence of metals in SSIX waters, suggests the presence of approximately 235 mg/L (as $CaCO_3$ equivalent) of pH dependent weak acid. Weak acid only partially dissociates from its hydrogen ions, in contrast to the behaviour of a strong acid. The design of the AWTP is such that it can cope with irregular or extreme acidities, which may be caused by the acidity inconsistency identified here. However, it will be useful for Mt Tom Price Mine to be able to understand the potential presence of any organic acidity and thus be able to remove it or declare it during any future project consent applications.

One unproven hypothesis is that the SSIX pit water contains weak organic acids, generated by the seasonal algal blooms, which contribute pH dependent acidity during neutralisation. Alternatively the weak organic acid might be contributed from the SEP input to the SSIX pit.

1.2 Scope of thesis

1.2.1 Project Objectives

This project was initiated to characterise the acidity in the SSIX pit water and to investigate the potential presence of pH dependent weak acids and algal growth. Such knowledge will allow for a heightened understanding of the inconsistencies between titratable and calculated acidity ultimately facilitating optimisation of the AWTP operation and further site investigations.

The primary objective of this thesis is to determine if the weak acid presence is caused by SEP pit drainage or the SSIX algae. From this knowledge a more complete understanding of

the hydrological, hydrogeological and biological systems related to the SSIX pit will be developed.

Additional objectives of this thesis include:

- Determination of the source and relative characteristic contribution of weak and strong acids in the SSIX pit and SEP pit water chemistry.

- Investigation of the physical and biological factors influencing successful algal growth in SSIX pit and an understanding on the potential for algal or bacterial growth to generate organic acidity in the system.

- Investigation of the potential presence of organic acid in SSIX pit and determine whether it independently controls the acidity inconsistencies of the SSIX pit.

- Recommendation of approach for the removal of the conditions for successful growth of algae in the SSIX pit (or use an algaecide) to aid its removal (or control further growth), making it possible to potentially reduce the overall acidity load and the amount of lime required by the acid water treatment plant.

1.2.2 Thesis format

Chapter 1- Introduction and Background

A background and scope of the thesis project will be acknowledged along with specific information relating to physical site characteristics.

Chapter 2 – Literature Review

Relevant aspects surrounding the project are recognized and comprehensively understood from previous knowledge and complimentary literature.

Chapter 3 – Sampling and laboratory analysis methods

Standard methods of sample collection by RTIO are used, along with those of commercial labs for geochemical analysis, as necessary. Reasoning is also provided for the chosen

standards and techniques that have been personally used to analyse the acidity inconsistency in this thesis.

Chapter 4 – Analysis of archived RTIO and Environmental Monitoring Data

The organisation and presentation of results, encompassing each aspect of the project through the use of RTIO archived raw data and environmental monitoring raw data.

Chapter 5 – Analysis of 2012 samples and laboratory results

The organisation and presentation of results collected in 2012 for this thesis and analyses of both personal and commercial laboratory work.

Chapter 6 – Characterisation of the SSIX pit acidity inconsistency

Further discussion and comparison of the results from Chapters 4 and 5 and the identification of key findings.

Recommendations are also made towards Mt Tom Price mine for the removal of the acidity inconsistency issue in the SSIX pit, in relation to project findings and complimentary literature.

Chapter 7 – Conclusions

Concluding statements on key findings from the thesis and recommendations for future work.

1.3 Location and Environment

1.3.1 The Pilbara

The Pilbara region of Western Australia is a vast landscape, which features coastal plains, inland ranges and contains some of the earth's oldest rock formations and important mineral deposits thought to be around 3.5 billion years old (ANRA, 2002). Economically the region hosts a number of significant national parks, but its infrastructure depends on the mineral wealth related industries of its region. The Pilbara now significantly contributes to Western Australia's economy by providing the states three largest exports, petroleum, natural gas and iron ore (gold mining is also becoming an important industry; ANRA, 2002).

The Hamersley Basin, located in the Pilbara, holds Australia's largest reserves for iron ore. Due to the increasing global market for iron ore, there are 14 Rio Tinto iron ore mines in operation in the Hamersley Basin with future development already in place. There are also several other, but separately owned, mines in the region and the mining plans, as laid out in Figure 1.1, are continuously changing.

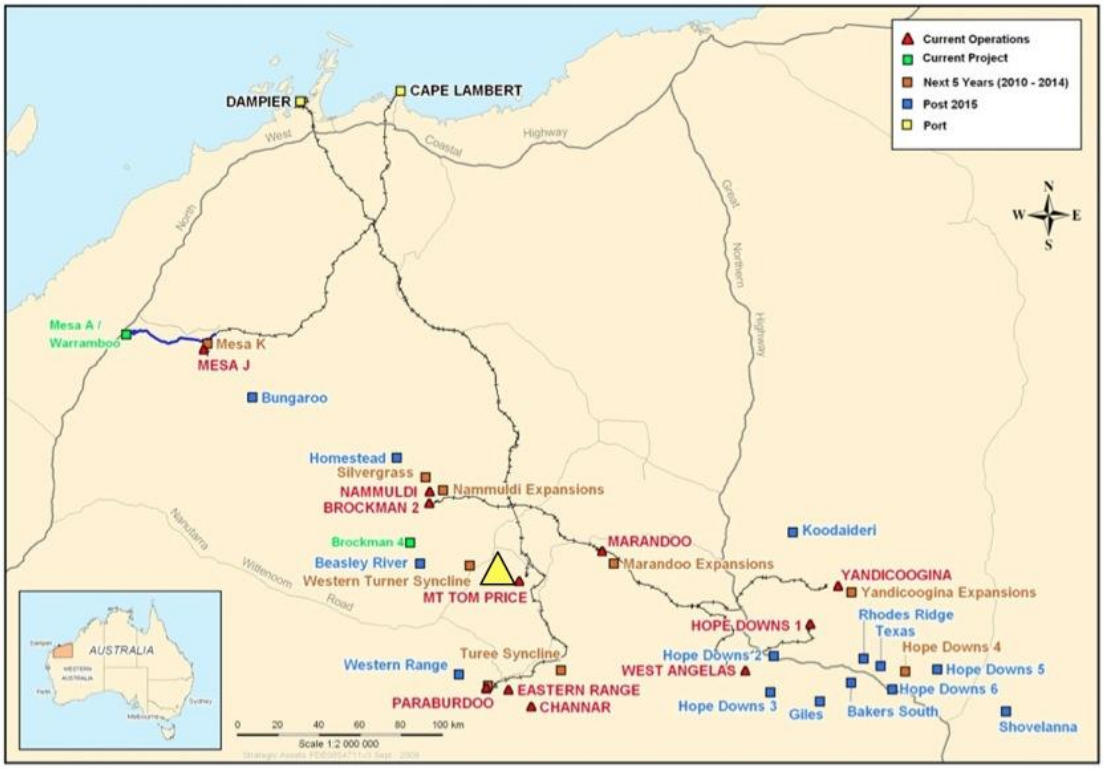


Figure 1.1 Current and projected ore operations in the Hamersley Basin as depicted by Walsh (2010) . NB. These plans are always changing and the expansions presented here may not occur as predicted. Mt Tom Price Mine shown by yellow triangle.

1.3.2 Mt Tom Price Mine

Located roughly 1400 km north of Perth and with an area of 60 km^2, Mt Tom Price mine is just one of the many iron ore mines owned and operated by Rio Tinto Iron Ore (RTIO) in the Hamersley Basin (Figure 1.1).

Mt Tom Price mine was the first RTIO mine to begin iron ore production in the Pilbara, with its first year of operation in 1966. The mine operates out of the established town of Tom Price (population 2700, not including the additional fly in/fly out population), as one of the only mines in the Pilbara with residential workers (RTIO, 2012b).

Mining extended below the water table in 1998, when dewatering via production bores began in the SEP pit (Staines and Buller, 2012). This below water table exposure of ore and other associated material generated acidic surface water within the pit. Acid water accumulated further during cyclone flooding (Cyclone Monty 2004) and site personnel initiated the transfer of acid water to SSIX pit for storage and evaporation. The occurrence of this acidic water generated on mine site is classified as Acid and Metalliferous Drainage (AMD).

Mt Tom Price mine quickly became the only RTIO site in the Pilbara producing a considerable volume of AMD. The need for an on site treatment system became necessary and the AWTP was installed in 2007.

1.3.3 Local climate

Located in Western Australia, the Pilbara is typically an arid to semi-arid region (with a Köppen climate classification of BWh; Briggs and Smithson, 1986). This climate is influenced by the Indian Tropical Maritime air from the west and the tropical continental air inland (ANRA, 2002). These two systems aid the potential for droughts or tropical cyclones in the region, within two distinct seasons. Wet summers have most of the rainfall between December and March and dry winters have a distinct period between August and November.

The Tom Price meteorological station (number 005072; Bureau of Meteorology, 2012b) recorded an average temperature for each month from 1997-2011, with the maximum average during January at 38.3 °C and the minimum average during July at 23 °C. However the demanding work environment is also known to regularly reach temperatures above 40 °C in the summer, with the highest daily temperature recorded reaching 45 °C (Bureau of Meteorology, 2012b).

Evaporation rates in the region can reach very high levels during the summer months, with the annual evaporation rate at approximately 2500 mm (ANRA, 2002). Figure 1.2 shows how this produces the largest deficit between precipitation and evaporation during the months of July to November (Manewell, 2008).

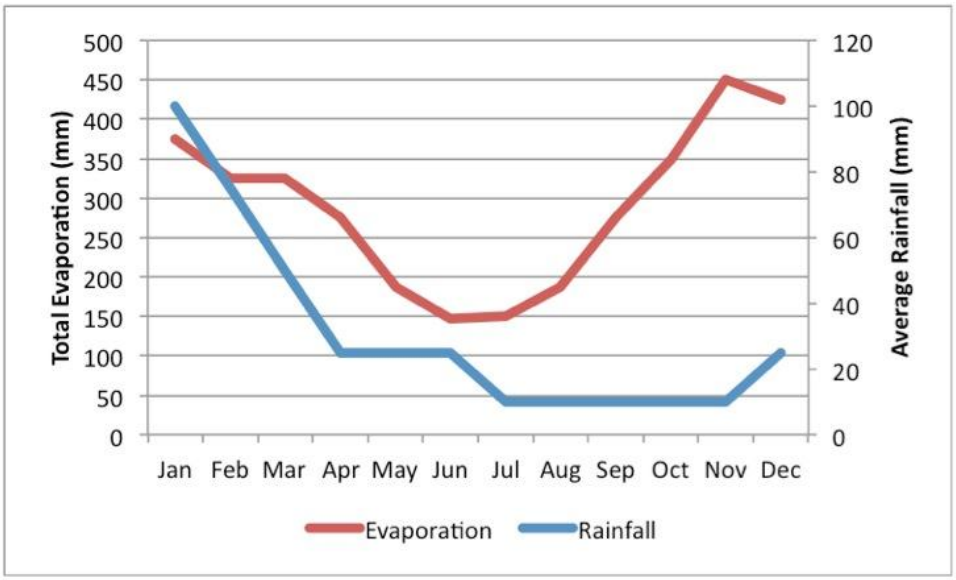


Figure 1.2 Comparison of average evaporation and rainfall data from Mt Tom Price area (adapted from data; Bureau of Meteorology, 2012a)

Average annual rainfall can vary from 200mm to 350mm, however large variability can occur year to year due to the intense wet seasons or cyclones in summer (ANRA, 2002).

Cyclones hit the area about seven times every decade and contribute 40-60 % of the regional rainfall (ANRA, 2002). Although many cyclones have certainly occurred in the Pilbara in the past, the following rainfall record from Tom Price (Figure 1.3) illustrates how Cyclone Monty produced exceedingly high rainfall at Tom Price, with 140 mm on March 3rd 2004 (Bureau of Meteorology, 2012b). Cyclone Monty is the most relevant event to this project because the flooding initiated the need for excess surface water to be pumped to the SSIX pit. In addition Figure 1.4 shows an observational view of the flooding that occurred in the SEP pit.

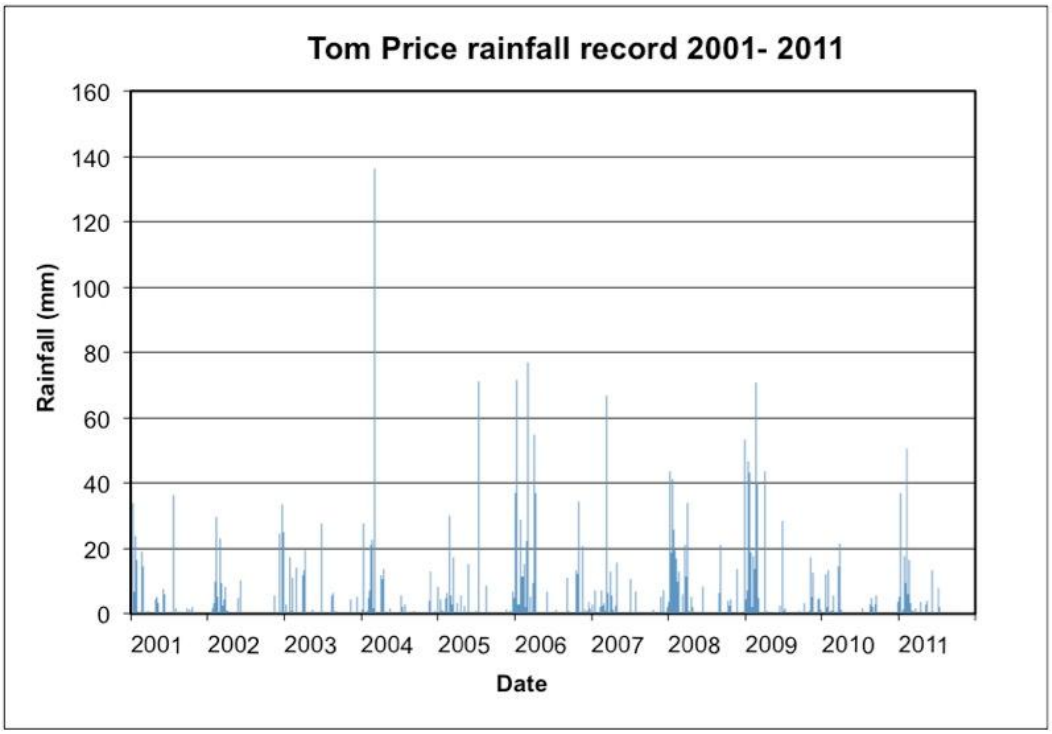


Figure 1.3 Rainfall record at Mt Tom Price mine, shows high rainfall during Cyclone Monty in 2004. (Figure courtesy Ed Buller)

Figure 1.4 Comparison of aerial photos showing presence of surface flooding in the SEP pit. Left - A 'normal' aerial view of the SEP pit in late 2004. Right - Aerial photograph of surface flooding in the SEP Pit caused by Cyclone Monty in 2004. (Google Earth. 2012).

1.3.4 Geology

The Geology in the Pilbara region is characterised by the formations in the Hamersley Basin known as the Hamersley Group. The Hamersley Group (Figure 1.5) is approximately 2.5km thick and contains five major banded iron formations (BIF). BIF is typically seen as bands of iron minerals (hematite and magnetite) and gangue minerals (mostly carbonates and cherts). Those BIF that have undergone supergene enrichment (where the iron content of the BIF is

increased due to the action of groundwater percolating through the bedding planes and joint fractures; Hedley, 2009) are high-grade iron mineralisation deposits (>60% Fe). Together, within the Hamersley Group, the Brockman Iron Formation and the Marra Mamba Iron Formation host numerous deposits of high grade iron mineralisation (Hamersley Iron, 2000), of which all RTIO mines in the Pilbara target.

1.3.1.4 Brockman Iron Formation

The Brockman Iron Formation, a highly enriched BIF, is the most economically important formation in the Hamersley Region. The low phosphorous content at Tom Price is particularly appealing for steel making. The formation can be divided into four primary members, Yandicoogina Shale, Joffre, Whaleback Shale and Dales Gorge (Hamersley Iron, 2000). The Mt Tom Price mine iron ore deposit is primarily excavated from the Dales Gorge member of the Brockman Iron Formation. However, within the last couple of years the Marra Mamba formation has also been mined.

The Dales Gorge member is approximately 150m thick, with an assemblage of 17 BIF macrobands and 16 shale macrobands varying from 1 m to 25 m thick (Cook and Shergold, 2005; Hamersley Iron, 2000). The member has been informally divided by Hamersley Geologists into three units (Dales Gorge 1, 2 and 3), which classify ore grades according to shale content. High grade ore comes from Dales Gorge zones 1 and 3 (Hamersley Iron, 2000).

The deposit at Mt Tom Price contains the second largest reserve of high-grade hematite ore in the Hamersley region, with an original resource of 900 Mt of almost pure hematite (averaging 63.9% Fe). The current resource is now 200 Mt and reaches an annual production of 28 Mt (RTIO, 2012a; Thorne et al., 2004).

The Mt Tom Price deposit extends for seven kilometres from the North Deposit to the SEP deposit (from the NW to the SE). The deposit is up to 1.6 km wide (averages 600 m wide) and 250 m below the surface.

1.3.2.4 Mt McRae Shale

The Mt McRae Shale formation is exposed on the pit walls due to local synclinal folding as well as at the base of production at Mt Tom Price mine, due to the sharp boundary below the Brockman Iron Formation's Dales Gorge member.

Prior to below water table mining, exposures of unoxidised Mt McRae Shale were rare in the Pilbara and Mt Tom Price was the first to deal with the consequences of its exposure. The Mt McRae formation is around 90 m thick and includes shale, siltstone, dolomitic shale and thin beds of jaspillite and chert (Hedley, 2009). The shale sediments are easily erodible and have the potential to contain abundant pyrite, which is acid forming when oxidised and has the ability to spontaneous combust.

1.3.5 Hydrogeology

Bedrock groundwater flow has dominated the hydrogeology at Mt Tom Price mine (Figure 1.6), with the main aquifers occurring within the ore bodies and a general SW flow through discontinuities in the tight BIF and shale units. Areas where mineralisation and faulting have increased permeability, has also resulted in some perched water bodies and clustered areas of radial groundwater flow in the mining area (Manewell, 2008). The removal of the more permeable units (being the higher grade ore mineralisations) and increased permeability by the removal of overburden loads has been caused by the past 40+ years of mining and will continue with future mining (Manewell, 2008). There is a potential for seepage from SSIX toward the SW, bores and monitors are in place to investigate this (please see SSIX pit site description 1.4.2). A current view of the hydrogeology at Mt Tom Price mine can be seen in.

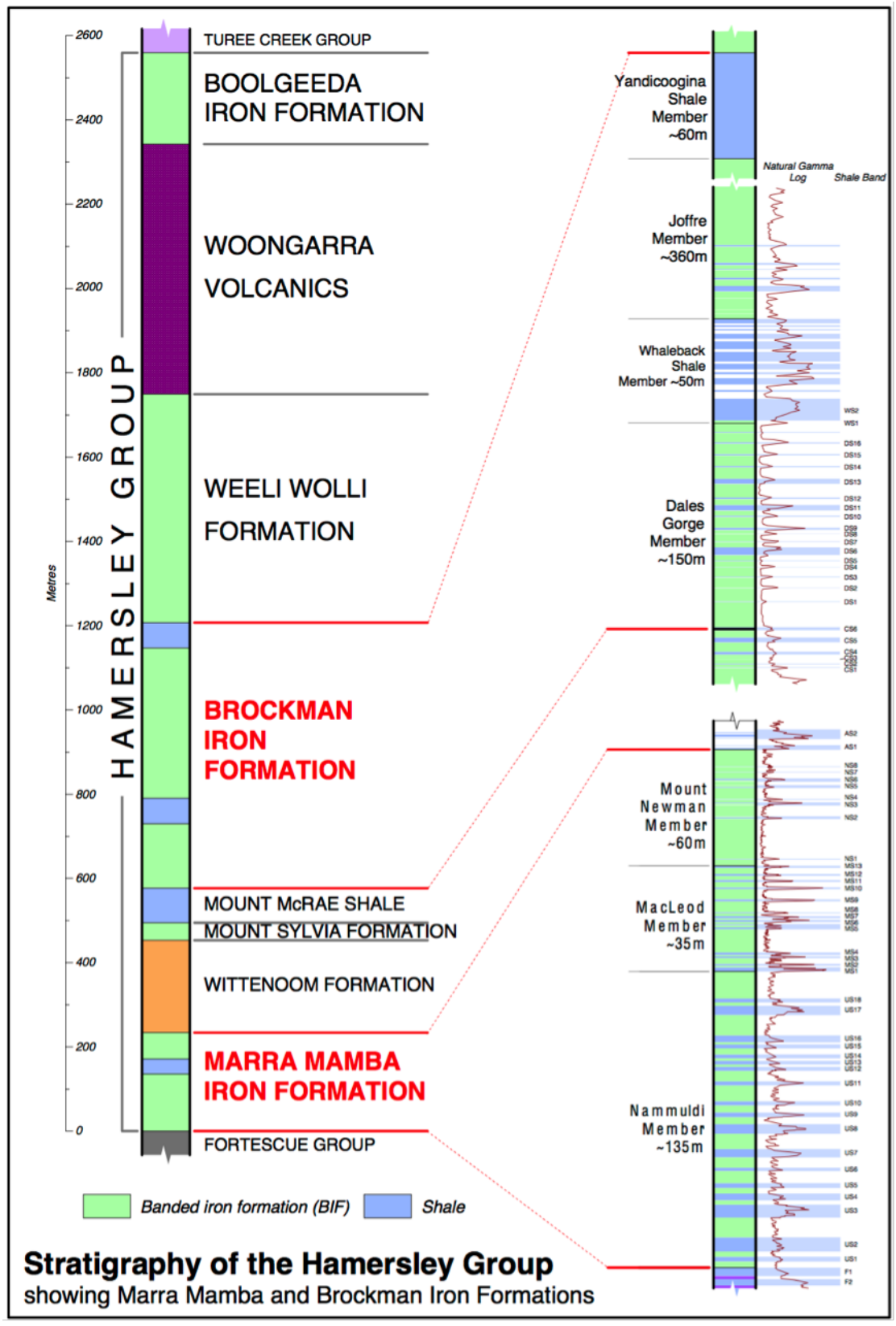


Figure 1.5. Stratigraphy of the Hamersley Group. Showing the Brockman Iron Formation and its Dales Gorge member (Hamersley Iron, 2000).

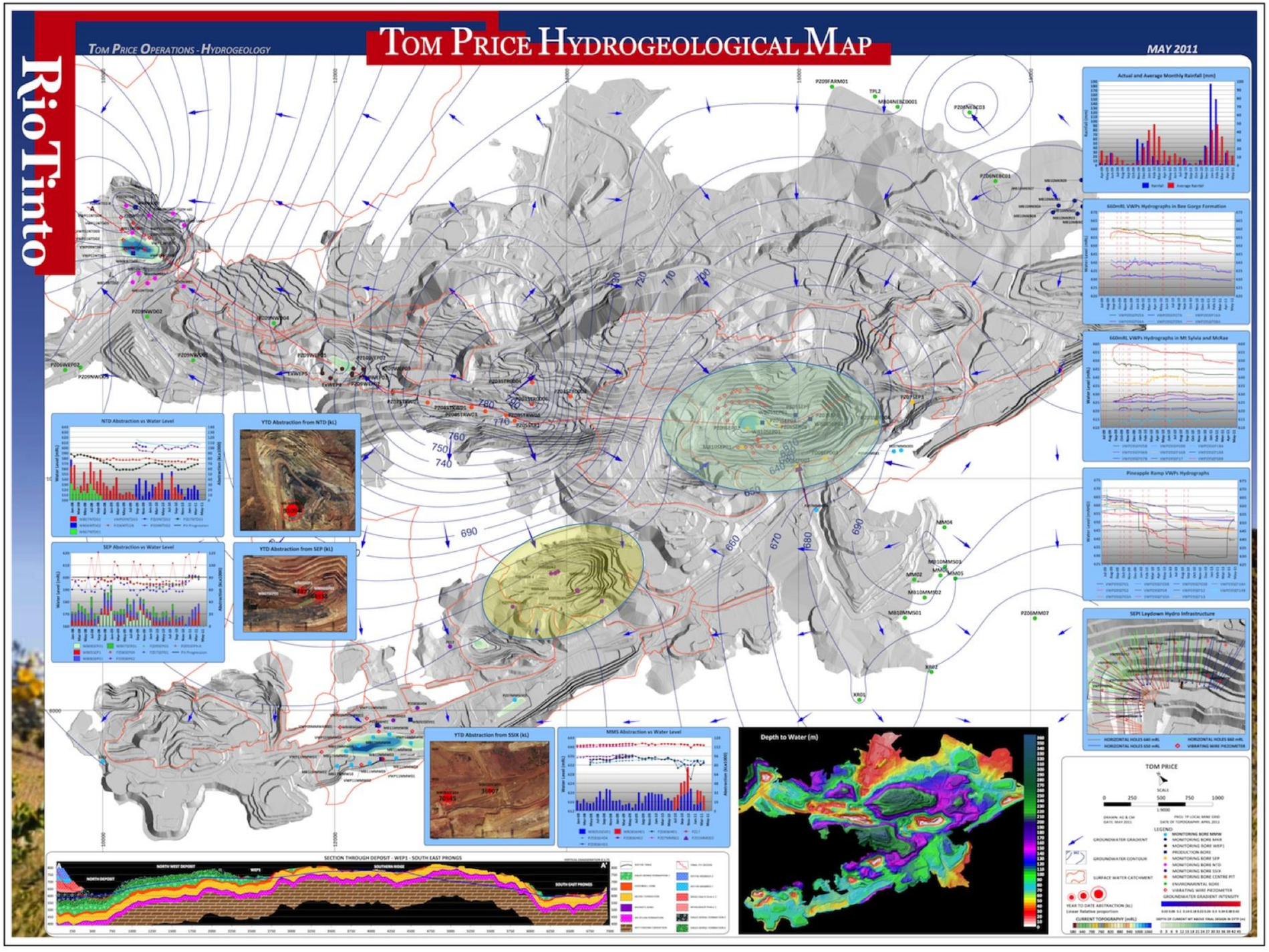


Figure 1.6 Tom Price Hydrogeology map. Highlighted – SSIX (yellow) and SEP (green). Map supplied by Steven Lee, RTIO Project Geologist, 2012.

1.4 Site Descriptions

This project will focus on the surrounding inputs, outputs and monitoring of environments of the SSIX pit at Mt Tom Price mine. The relevant site descriptions related to SSIX are presented in the following sections.

1.4.1 The South East Prongs Pit

The SEP pit at Mt Tom Price mine is one of the largest open cast mining pits in the Pilbara region (Figure 1.7 and Figure 1.9). The SEP deposit within the pit, is the largest ore body at Mt Tom Price mine as a 1.0 km by 0.3 km synclinal structure, with high grade mineralisations of the Dales Gorge member present to a depth of 250 m (Manewell, 2008).

Mt McRae Shale is present in the SEP pit wall and is therefore exposed to oxidation, resulting in highly acidic runoff into the ephemeral pit lake.

Mining in SEP extended below the water table in 1998, when dewatering via production bores began. The groundwater table has since dropped its pre-mining height of ~674 mAHD (meters Australian Height Datum) to beyond 630 mAHD and the SEP pit is now an area of intense pumping (Hedley and Dogramaci, 2010). Currently there are multiple active pumps operational at any one time, each pumping volumes between 420–5160 kL/day on average (Manewell, 2008).

After Cyclone Monty, in 2004, it was estimated that 116 ML of surface water had accumulated in the SEP pit (Figure 1.4). It is also known that during the cyclone the groundwater table was only 5 m below the pit base and the potential for groundwater contamination by surface run-off was acknowledged; but no data had yet proven this (Hedley and Dogramaci, 2010).

In order for production to recommence in the SEP pit, RTIO (then known as Hamersley Iron) obtained permission for a one-off transfer of low pH surface water from the SEP pit to SSIX pit, which occurred during 25 March and 5 May 2004 including relocation of 97 ML of acidic water. After this one off discharge it was decided that further surplus acidic dewatering and surface water generated from SEP pit would continue to be discharged to the SSIX pit via a network of pumps.

1.4.2 The Section Six Pit

SSIX is located on the southern arm of the broad regional synclinal feature that hosts all Tom Price ore bodies (Figure 1.8 and Figure 1.9). SSIX consists of one small pit, which was originally excavated for ore and had one pump operating from 1994-2003 (now known as WB05SSIX1), which extracted on average 490 kL/day (Manewell, 2008). As previously stated the SSIX pit is now the discharge location of acidic water from dewatering and depressurisation bores in the SEP, as well as the SEP pit surface water following major rainfall events (since Cyclone Monty in 2004).

Prior to the decision to utilize the retired SSIX pit for acidic water storage from the SEP pit, the main constituent of surface water in the SSIX pit was sourced from groundwater seepage. Evaporation of this surface water resulted in high chloride concentrations and total dissolved solids (TDS) of 11,000 mg/L (Hedley and Dogramaci, 2010).

Once the continual water input from the SEP pit began, the hydraulic gradient reversed causing local groundwater levels to rise. Piezometers located within the pit showed a rise of ~5 m over six months, due to the water level in the pit being relatively higher than the surrounding groundwater (Hedley and Dogramaci, 2010). Thus, SSIX switched from acting as a natural discharge location to an artificial recharge zone.

Mt McRae Shale is also present in the pit wall of the SSIX pit and is therefore exposed to oxidation reactions above the pit lake. The modelled black MCS exposures cover 18,600 m^2 in the SSIX pit (Figure 1.10), with the upper extent located at 680 mRL and all exposures below the pre-mining water table (Terrusi, 2013). Runoff produced from the shale likely contributes to additional acid generation in the storage pit lake (Gallagher, 2012).

Seepage from SSIX into the surrounding groundwater was not initially believed to be an issue of concern when the pit was chosen for storage, because of the low permeability of rocks in the pit (Hedley and Dogramaci, 2010). However the following graphs (Figure 1.11 and Figure 1.12) show the physical and chemical correlation between surface water in the SSIX pit and surrounding SSIX groundwater (Hedley and Dogramaci, 2010). This is possibly due to fractures in the rock facilitating for water transfer/seepage. Once water has been collected in the SSIX pit from both SEP and SSIX surface water, it is generally pumped weekly to the AWTP for neutralisation.

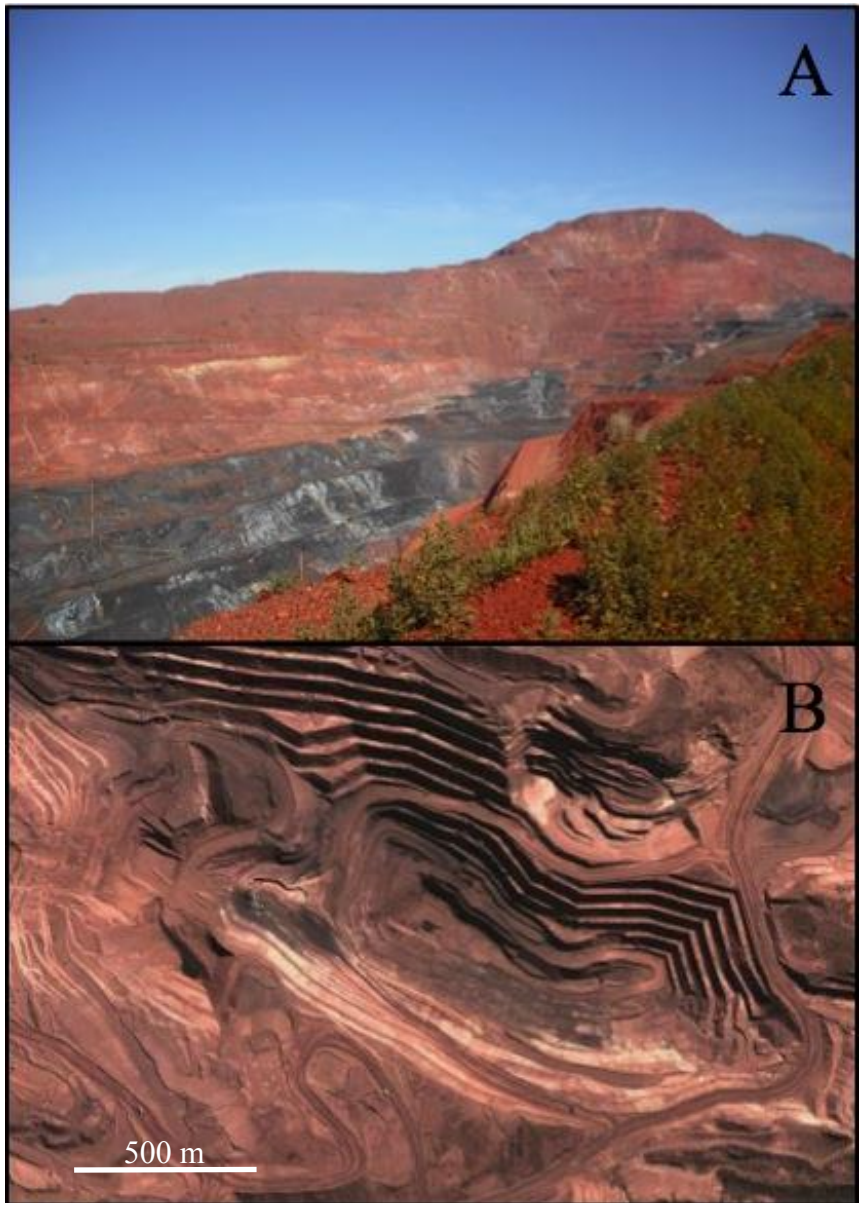


Figure 1.7 (A) South East Prongs Pit landscape view. (B) South East Prongs Pit aerial view. (April 2012, Mt Tom Price Mine, WA; Google Earth, 2012).

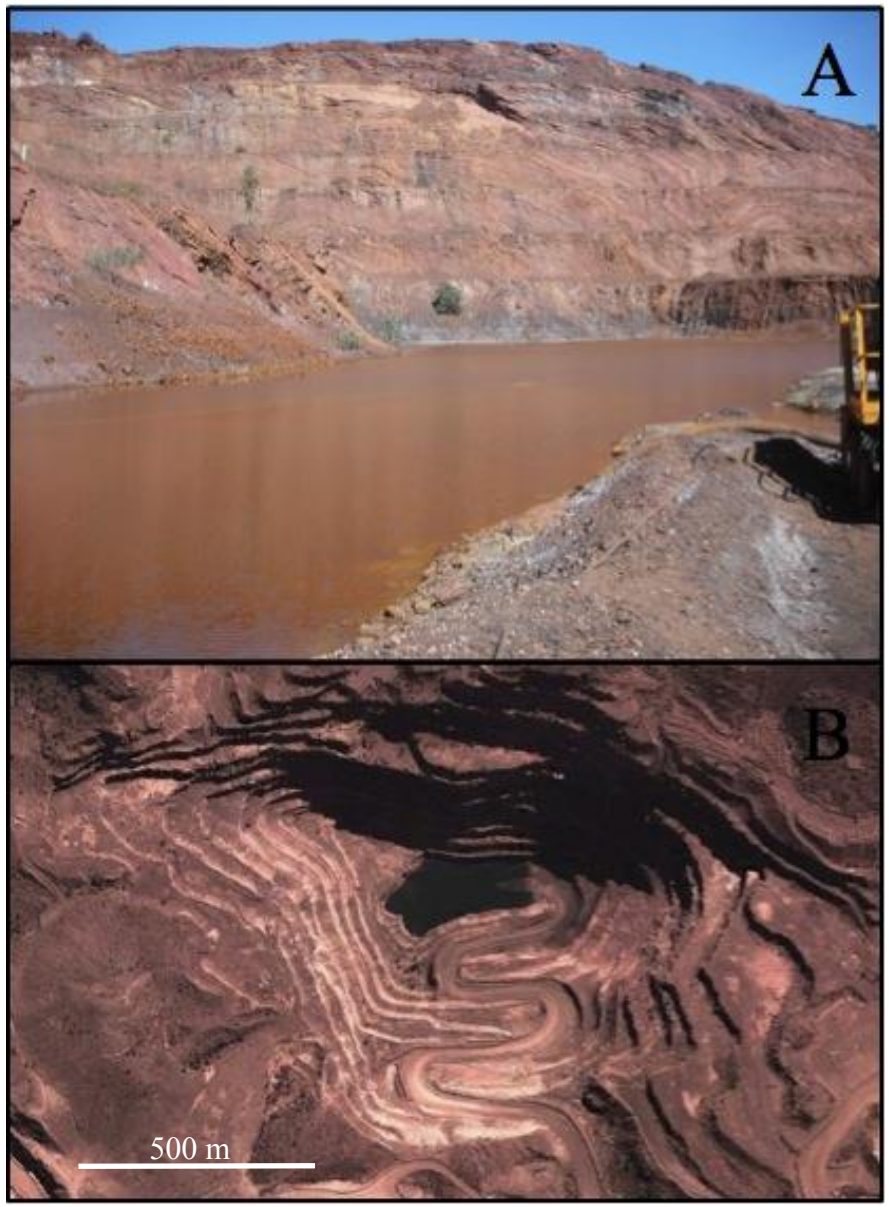


Figure 1.8 (A) Section Six Pit Landscape view. (B) Section Six Pit aerial view. (April 2012, Mt Tom Price Mine, WA; Google Earth, 2012).

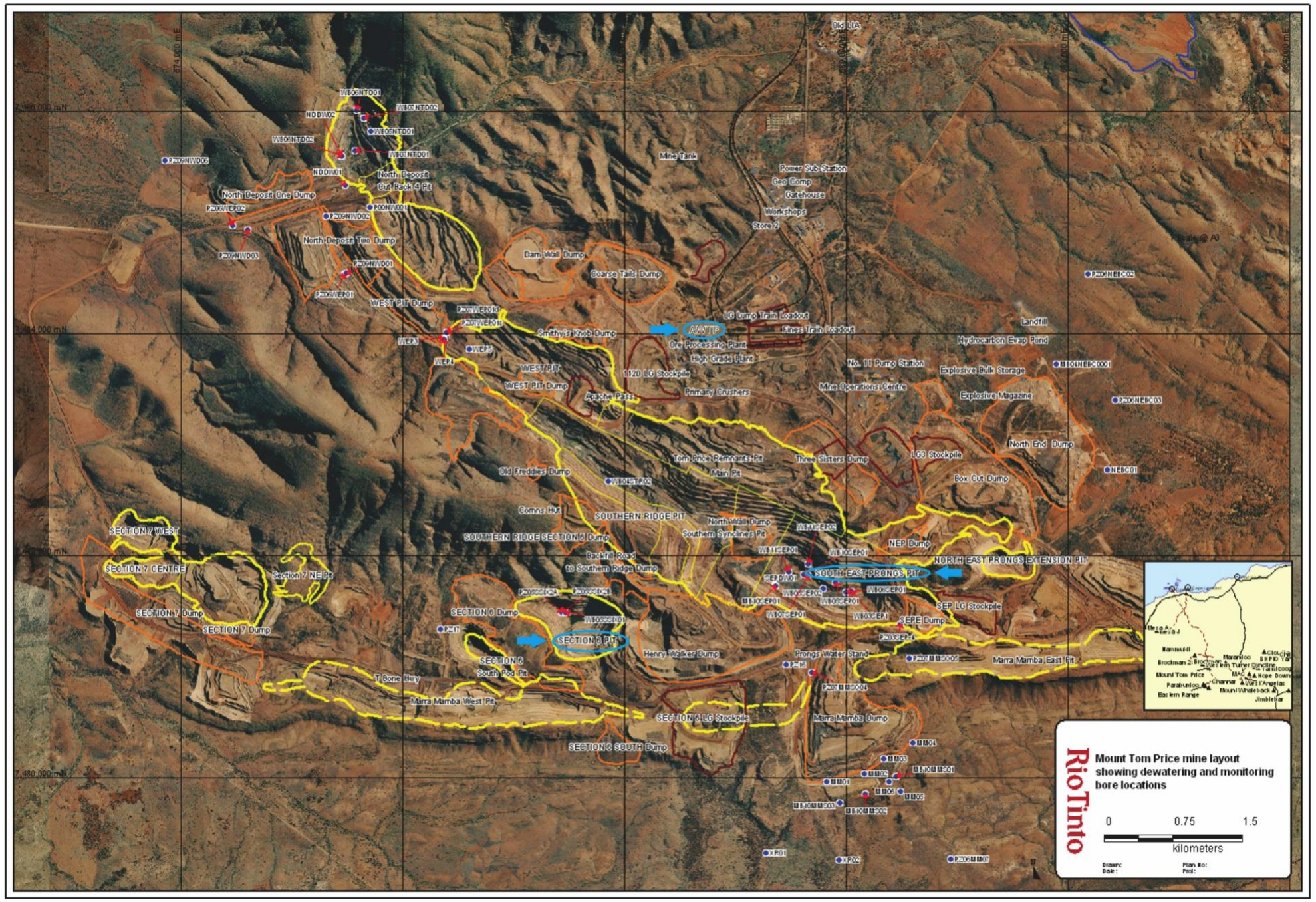


Figure 1.9 Mount Tom Price Mine layout showing dewatering and monitoring bore locations and (in blue) SSIX, SEP and the AWTP (Staines and Buller, 2012)

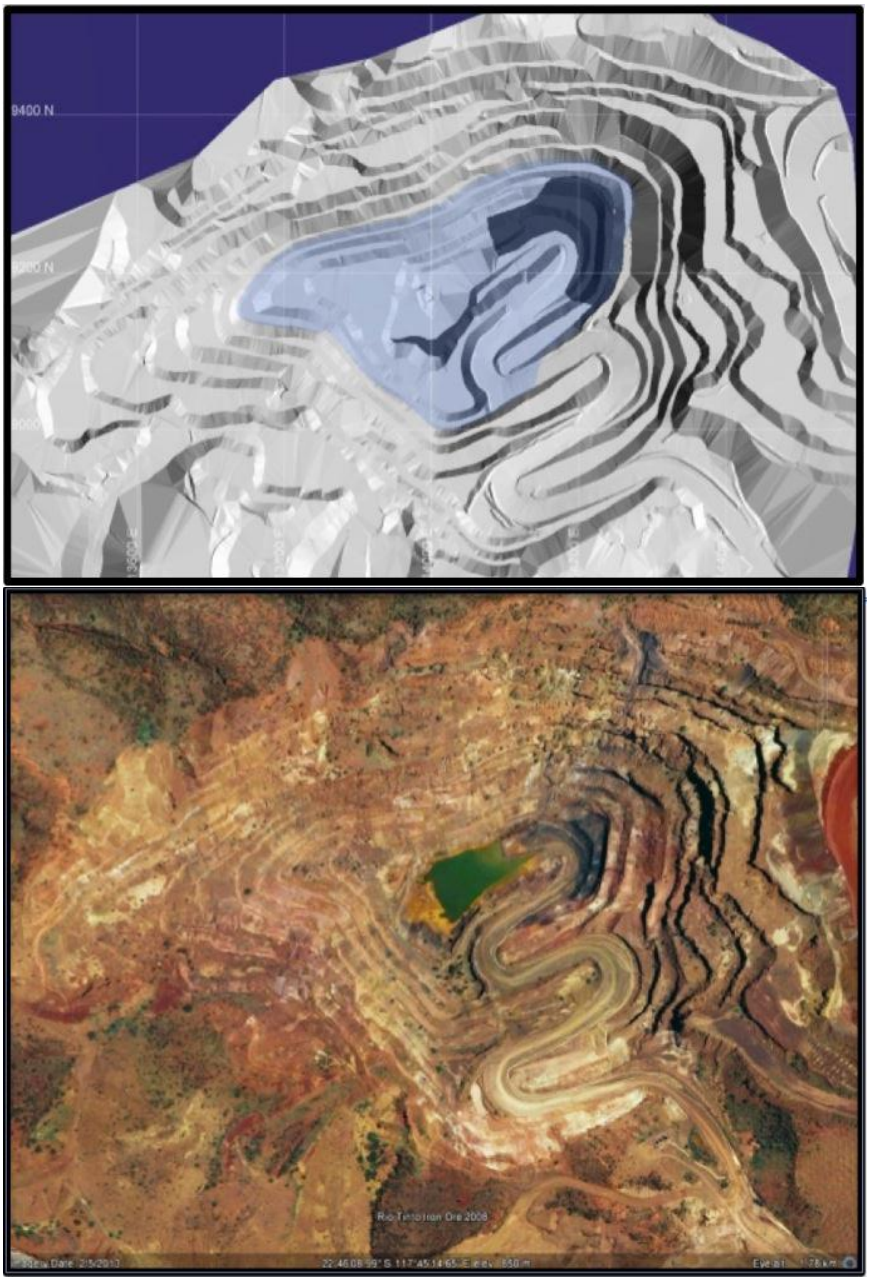


Figure 1.10 (Top) Modelled exposures showing the location and extent of the MCS (black shading) in the SSIX pit, based on aerial photograph (below). The modelled pre-mining water table (blue shading) is also shown (Terrusi, 2013).

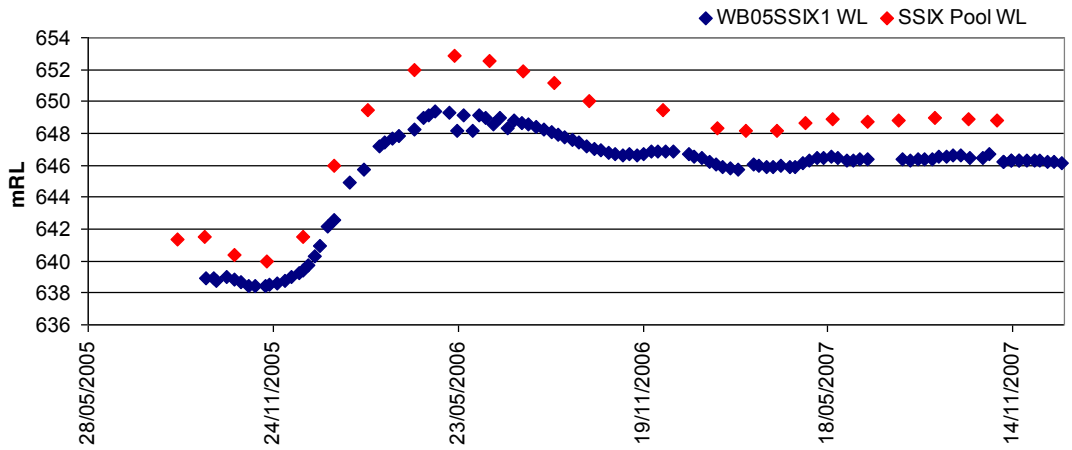


Figure 1.11. Groundwater level in SSIX bore (WB05SSIX1) versus SSIX pit water level (Hedley and Dogramaci, 2010)

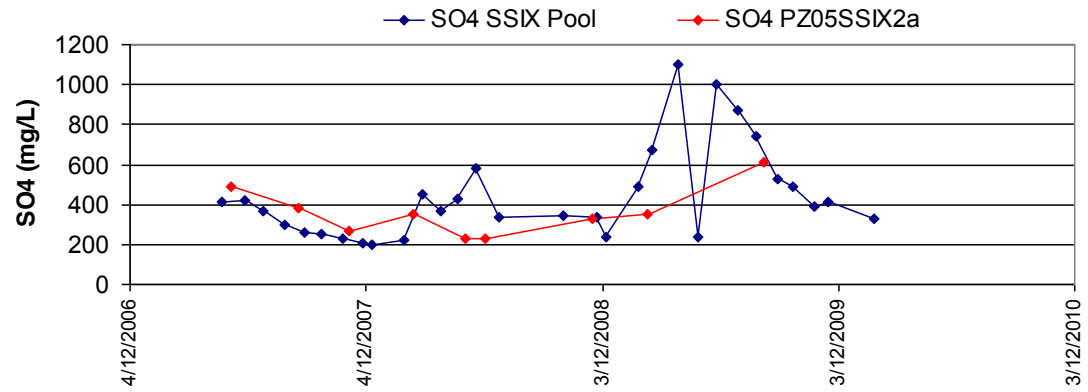


Figure 1.12 Relationship between the SO_4^- concentrations of the shallow bore PZ05SSIX2a and SSIX Pool. (Hedley and Dogramaci, 2010)

1.4.3 Bores

The following list contains the names of bores that are surrounding inputs to the SEP pit and subsequently the SSIX pit, thus related sites in this thesis. These bores are used for data collection by RTIO for environmental monitoring. Most of these bores can also be seen labelled in there physical locations on Figure 1.9. Some of these bores will be used for further results analyses (and in appendices) of water samples that have been collected over time (since 2002) by the Environmental Monitor.

South East Prongs bores:

1. SEP (DB3) / SEPDW01 (duplicate names)
2. WB03SEP01

3. WB05SEP01
4. WB05SEP02
5. WB06SEP01
6. WB07SEP01
7. WB10SEP01
8. WB11SEP01
9. WB11SEP02

Section Six bores:

1. SSIX MM01
2. WB05SSIX01
3. PZ17
4. PZ05SSIX2A
5. PZ05SSIX2B

Relevant Surface Water Monitoring Points are:

- SSIX pit / Section 6 Pond / SSIXPOND (duplicate names)
- SEP pit / SEP Surface Water / SEP Pit-Surface Water (duplicate names)
- SEP Cyclone Tank

1.4.4 The Acid Water Treatment Plant

Due to excessive acid water accumulation (from Cyclone Monty in 2004) and the continual exposure of Mt McRae Black Shale in the SEP pit (due to mining progression), the decision was made to build an onsite acid water treatment plant to treat and reuse the AMD water for onsite mining operations. If waste water were to be stored and treated in the SSIX pit there would still be potential for waste water to leak from the pit.

In 2007, the AWTP was constructed on site as a typical low density sludge neutralisation plant, consisting of two reactor tanks that add powdered lime to raise the pH of the solution and precipitate soluble metal ions (Buller, 2011). However, the predicted volume of AMD generation was overestimated during the design process, resulting in there only being enough AMD to run the AWTP once a week.

Plant operation during times of fluctuation in water quality, such as the first rain of the wet season, can be complex. To manage this AMD is stored in SSIX pit thereby buffering out most issues related to fluctuation creating a more manageable variation of flow to the AWTP.

1.5 Summary

This chapter presents a thorough scope for this thesis along with the project objectives.

Each section has highlighted the background information that will be required for the detailed investigation presented in this thesis. This information includes:

- The relative climate of the Pilbara and the cyclones that effect Mt Tom Price Mine
- The local geology surrounding Mt Tom Price mine, and its inclusion of the pyrite bearing Mt McRae shale, which causes generation of AMD.
- The relative Hydrogeology in the Mt Tom Price area, for recognition of potential seepages of AMD.
- The site descriptions of the relative locations and catchments of interest in this thesis.

This thesis will investigate the multiple ecosystems factors, across each aspect mentioned in this chapter, to focus on the direct and non-direct effects controlling the acidity inconsistency issue of the SSIX pit.

2 Literature review

2.1 Introduction

This chapter discusses published scientific principles that relate to the issues of AMD in the SSIX pit of Mt Tom Price, particularly in relation to the acidity inconsistency and algal blooms previously identified in 2007.

The sections discussed in this chapter explore the theory behind AMD, with a focus on geochemical analyses used to identify chemical species and properties in a water sample, as well as the use of titrations to further understand acidic species in solution. Characteristics of algal blooms in acidic environments are also discussed. These principles will also construct the reasoning for the methods in this project, to analyse the acidity inconsistency and algal bloom presence.

2.2 Acid & Metalliferous drainage (AMD)

The weathering of pyrite (and other sulphur-bearing minerals) when exposed to an oxygenated environment and water, causes the largest and most challenging environmental problem facing the mining industry today - acid and metalliferous drainage (Lottermoser, 2010). The resulting AMD conditions can contaminate water bodies potentially leading to inhospitable environments for many organisms (Das et al., 2009).

Acidic water can also occur in natural environments (i.e. non-human impacted). Such conditions are best described as acid rock drainage (ARD). The natural process of sulphurous mineral weathering is much slower than in human impacted systems, permitting the potential for long term adaption of aquatic ecosystems to the slowly acidifying aqueous environment, thus creating far less of an environmental impact (Kitto, 2009). However, anthropogenic acidic water bodies cause environmental problems because most organisms (other than certain algae and bacteria) cannot tolerate the rapid generation of strongly acidic water, along with the many toxic trace elements (heavy metals) that become mobilised under the strongly acidic conditions (Drever, 1988).

Sulphide minerals, the primary sulphurous minerals from which these acidic conditions originate, are produced under strongly reducing conditions and constitute a major proportion

of rocks of economic interest (particularly metal ore deposits), with pyrite (FeS_2) being the most common sulphide to be found in the Earth's crust (Lottermoser, 2010).

Environmental concerns associated with sulphide weathering have only increased in recent decades as open cast mining operations look to increase their production by extending mining operations below the water table. In order to do this safely, and reduce the risk of slope failure, the groundwater table must be lowered by pumping, often through a network of bores drilled into the area within and surrounding the mine site. The subsequent exposure of un-oxidised, below water table minerals facilitates sulphide weathering and thus AMD.

Regardless of whether such pumping induced AMD conditions occur during mine operation or after mine closure, the AMD condition must be monitored and controlled in order to reduce the potential impacts on the environment.

Large volumes of sulphides can be exposed across many different aspects of mine structure, whether it be from the tailings dam, waste rock dumps, low-grade stock piles, open-pit floors and faces, road cuts, quarries or other rock excavations on site (Lottermoser, 2010). AMD is a widespread issue, which needs containment before treatment. Management systems can be put in place to prevent AMD. Initially it is very important to be able to geochemically characterise the risk posed by potential acid forming material. Section 2.3 (below) will discuss what geochemical analysis procedures are routinely carried out at Mt Tom Price to characterise total sulphur concentrations and to identify the boundaries between non acid forming and potentially acid forming materials. Information regarding remediation options if management is unsuccessful is also presented.

2.2.1 Formation

When mining exposes sulphurous material to an oxidising environment the minerals are removed from the water saturated (anoxic) environment and become chemically less stable, producing a series of complex chemical weathering reactions. This results in an acid-water laden with sulphate, heavy metals (such as iron, aluminium and manganese) and metalloids. Metalloids are chemical elements that resemble both metal and non-metal properties; for example, some elements will form amphoteric hydroxides that can contribute weak acids in solution (Whitten et al., 2007). Thus, presence/absence of these potential/amphoteric weak acids is in addition to any organic weak acids present in the system.

The principal sulphide minerals in most target materials are pyrite and pyrrhotite. However, this varies from different sites depending on location, with ZnS (sphalerite) and PbS (galena) also acting as commonly occurring sulphide minerals. Due to acidic conditions an additional release of metal elements from the host rock can occur, such as the release of aluminium, arsenic, cadmium, cobalt, copper, mercury, nickel, lead and zinc (Blowes et al., 2003). This is explained further in Section 2.2.3.

The formation of AMD can be caused by any of four processes or their combinations (Lottermoser, 2010):

- Oxidation by oxygen (abiotic direct oxidation)
- Oxidation by oxygen in the presence of microorganisms (biotic direct oxidation)
- Oxidation by oxygen and iron (abiotic indirect oxidation)
- Oxidation by oxygen and iron in the presence of micro-organisms (biotic indirect oxidation)

For the purpose of the example below, I focus on a four-step culmination of the processes above for the oxidation methods of pyrite (Buller, 2011; Moore, 2005), which in turn provides a cyclic production of AMD and a worst-case scenario.

Equation 2-1 shows the first step as the slow oxidation of pyrite (FeS_2) with oxygen and water, resulting in the formation of ferrous iron (Fe^{2+}) and the release of sulphate and two hydrogen ions causing an increase in acidity.

Equation 2-1 $$\mathbf{2FeS_{2(s)} + 7O_{2(g)} + 2H_2O_{(l)} = 2Fe^{2+}_{(aq)} + 4SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)}}$$

As acid begins to accumulate, the second reaction (Equation 2-2) continues by the oxidation of ferrous iron to ferric iron (Fe^{3+}) consuming one mole of acidity.

Initially this reaction is abiotic, but at a pH below 3 the reaction continues with biotic catalysation by the presence of the iron-oxidising acidophilic bacteria *Acidothiobacillus ferooxidans*, greatly increasing the production of acidity.

Equation 2-2 $$\mathbf{4Fe^{2+}_{(aq)} + O_2 + 4H^+_{(aq)} = 4Fe^{3+}_{(aq)} + 2H_2O}$$

Once the ferric iron is present (Equation 2-2), and the pH is below 3, direct oxidation of pyrite (FeS_2) by ferric iron can occur resulting in the production of much greater amounts of acidity (Equation 2-3).

Equation 2-3 $$FeS_2 + 14Fe^{3+}_{(aq)} + 8H_2O = 15Fe^{2+}_{(aq)} + 2SO_4^{2-}_{(aq)} + 16H^+_{(aq)}$$

Equation 2-4 then shows the final step, by which if the pH has raised above 3.5 (by either dilution or buffering of the AMD), the ferric iron readily precipitates as ferric hydroxide, which thus releases more acid.

Equation 2-4 $$Fe^{3+}_{(aq)} + 3H_2O = Fe(OH)_3 + 3H^+_{(aq)}$$

Once the pH drops below 3.5 again, some ferric iron remains in solution and continues to oxidise additional pyrite (as in Equation 2-3). The continued involvement of bacteria, during this indirect process, catalyses the reaction further and generates more Fe^{3+} - the major pyrite oxidant. Additional release of hydrogen and sulphate ions continue to lower the pH further in a biogeochemical feedback loop.

2.2.2 *Acidothiobacillus ferooxidans*

As discussed above, bacteria play a very important role in pyrite oxidation (and thus occurrence of AMD), by oxidising Fe^{2+} to Fe^{3+}. It is therefore important to understand the types of environments that these species of bacteria have the potential to occur in (such as the most commonly referenced *Acidothiobacillus ferooxidans)*.

Figure 2.1 shows three major factors that control the activity of *A. ferooxidans;* temperature, pH and oxygen concentration. The optimum temperature for *A. ferooxidans* activity is around 30°C, with diminishing activity at both higher and lower temperatures. A similar relationship is present for *A. ferooxidans* activity with respect to changes in pH, with the optimum pH at 3 and a cessation of activity below pH 1.5 and above pH 5. Jaynes et al. (1984) determined this declining behaviour, due to physiological limitations, was linked to the fact that bacterial oxidation of Fe^{2+} is limited below pH 2.5 (NB. alongside the limitation that pyrite oxidation diminishes over a pH 3.5 due to decreasing solubility of $Fe(OH)_3$). In the final relationship shown in Figure 2.1, it is determined that activity also ceases in the absence of oxygen, but also that these obligate aerobes (Evangelou, 1995) can resume activity even with increases in oxygen concentration as small as 0.01 mole fraction.

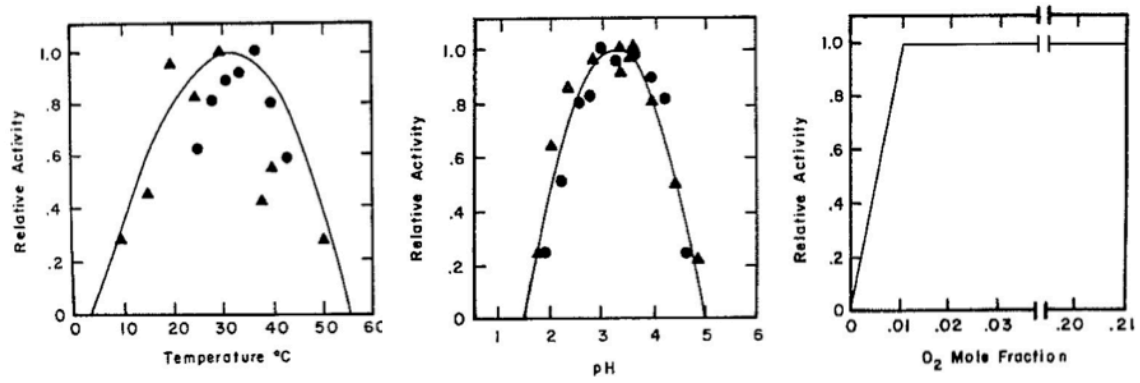


Figure 2.1 Influence of temperature (left), pH (middle) and oxygen concentration (right) on relative activity of *A. ferooxidans* (Jaynes et al., 1984).

Figure 2.2 presents an example of how bacterial activity is often temperature dependant, which in turn determines increased pyrite oxidation and AMD formation.

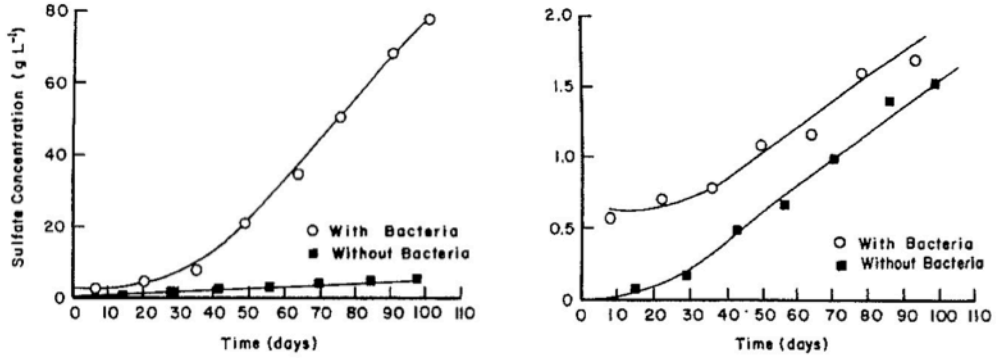


Figure 2.2 Pyrite oxidation kinetics in mine waste at 21°C and pH 3 (left) and at 6°C and pH 3 (right) in the presence and absence of bacteria (Jaynes et al., 1984).

2.2.3 Buffering and neutralisation

When AMD forms, gangue rock-forming minerals have the capacity to buffer much of the generated acidity by dissolving into solution and consuming the acidic hydrogen ions. Thus each dissolution reaction contributes to the overall acid neutralising capacity (ANC) of the rock. However, further contamination of the AMD is produced as the metal ions (within the gangue minerals) become dissolved into solution. For example, as seen in Equation 2-5, aluminium hydroxide can buffer an acidic solution by the uptake of hydrogen ions and thus dissolution to produce aluminium ions in solution and water.

Equation 2-5 $$Al(OH)_{3(s)} + 3H^{+}_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

These neutralising gangue minerals are largely non-economic and include (1) calcium and magnesium-bearing carbonates, (2) oxides and hydroxides of calcium, magnesium and aluminium, (3) soluble, non-resistant silicate minerals, and (4) phosphates (primary apatites; Sherlock et al., 1995). The weathering of these minerals occurred under the same oxidising conditions that the sulphides are subjected to (however buffering reactions are independent of the oxygen concentration in which the weathering reactions take place; Lottermoser, 2010).

Each type of gangue mineral undergoes hydrolysation within a different pH range. Once a certain buffering mineral is depleted the pH drops until the next most reactive mineral acts as the next buffer. Not all sulphidic wastes will produce AMD if there is an abundance of gangue minerals.

Figure 2.3 shows the order of reactivity of buffering minerals, carbonates (calcite, siderite), metal hydroxides (aluminium hydroxide, iron hydroxide) and silicates.

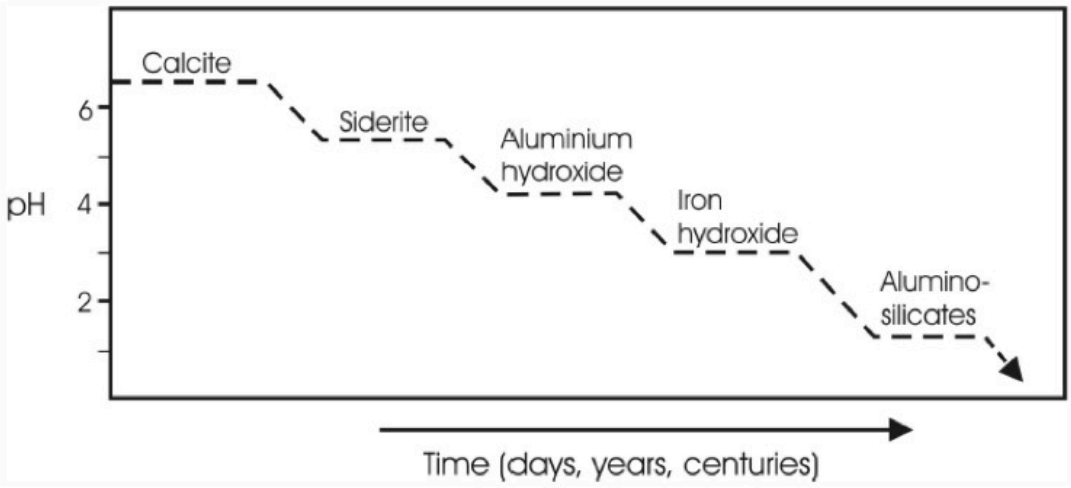


Figure 2.3 Consecutive buffering capacity of different gangue minerals in a hypothetical sulphidic waste dump (Solomons, 1995; cited in Buller, 2011; Lottermoser, 2010)

2.2.4 Impact

AMD is one of the main environmental issues surrounding the mining industry today, requiring significant quantification and management to determine its impact (Harries, 1997).

AMD typically occurs in catchments where the buffering/neutralisation capacity of the water body is low (Kitto, 2009). This status can have adverse effects on the freshwater communities, whether a direct lethal effect from the lowered pH and mobilised metal

toxicity, or through the interference of ecosystem processes. Both effects are usually correlated, by direct impacts eliminating sensitive species and causing reductions in diversity and density. Eventually affecting the food supply (causing top-down or bottom-up reactions through the ecosystem food web) and vital ecosystem processes (such as oganic matter decomposition, energy transfer and nutrient cycling; Kitto, 2009).

Dilution by downstream processes is not always beneficial to the situation, with pH increases causing iron precipitate to be released and settle on the streambed. Iron precipitate appears to be non-toxic to macro-invertebrates and periphyton but can smother substrate, reduce clarity and clog gills (Kitto, 2009). Limiting water to the impacted acidic system can reduce the production of AMD and cut off the primary transport mechanism (Buller, 2011).

In addition to the significant environmental impacts on mine site, AMD also creates large economic impacts. Waste management (e.g. prevention of AMD from tailings, waste rock dumps and exposed pit walls) can often account for as much as two-thirds of the total closure liability costs. This example comes from Newmont Australia's mining productions where the total estimated closure costs, for the sites that have a maintained financial interest, is in the order of $140 million (AUD), of which greater than 65% is for waste management (Dowd, 2005). This cost can potentially be much higher if AMD is discovered late in mine life or after mine closure. Therefore, it must be ensured that a proper waste management strategy is planned and in place by the mine owners and any financial liability will not be transferred to the government or community (Harries, 1997).

If left untreated AMD can persist for hundreds of years, until the sulphurous source is exhausted. Due to increased environmental awareness and changes in legislation over the last 20 years, mining operations are now expected to adequately treat or remediate AMD to reduce these foreseeable impacts (Kitto, 2009).

2.3 AMD at Mt Tom Price

AMD is present after large rainfall events in pit and groundwater production bores in the SEP and the SSIX pit lake, the study sites for this thesis. Section 1.3.4 presented the geological units at Mt Tom Price, which cause AMD, in particular the MCS sediments (shown in the stratigraphic column; Figure 1.5) that have the potential to contain abundant pyrite. In order to apply the scientific understandings of sulphide weathering processes to the conditions

present at Mt Tom Price mine it is first necessary to acknowledge the management and treatment of AMD on site.

2.3.1 AMD management

The pyrite bearing Mount McRae Shale (MCS), at Mt Tom Price mine, makes up a small proportion of waste rock and poses both spontaneous combustion and AMD risk (RTIO, 2010). Therefore the management of the MCS in turn directs prevention of AMD.

The risk posed by potential acid forming material at Mt Tom Price mine is determined with geochemical tests such as Acid Base Accounting and Net Acid Generation, which characterise total sulphur concentrations and can be used to identify the boundaries between non acid forming and potentially acid forming materials (Green and Borden, 2011). If mine waste is sourced from un-oxidised MCS (black shale), it is automatically classified as potential acid forming because of the unit's known pyrite content (Buller, 2011). This is a conservative approach as much of the upper MCS (top 14 m) has a sulphur concentration of less than 0.1% by mass and is most likely Non Acid Forming (NAF).

RTIO has devised a four-step management strategy to assess the risks of AMD as early as possible. This approach is taken such that appropriate pro-active management strategies can be selected and implemented. As detailed by Green and Borden (2011), the risk assessment process provides AMD hazard scores for selective areas of new production. The process includes assessment of environmental, human health, commercial and reputation risks with these four stages:

1. Preliminary AMD Hazard Score
2. Technical AMD and geochemical risk assessment report
3. Detailed AMD Hazard Score
4. AMD risk assessment of management strategies.

Each stage can be completed prior to mining, allowing full evaluations before any considerable investments or works have occurred, with the emphasis on prevention and minimisation rather than control and treatment where possible (Green and Borden, 2011).

The most common approach in the mining industry, for managing sulphurous wastes, is to install a low-permeability cover over wastes, usually constructed by compacting other mine wastes with an average costs of $40,000 per hectare (Harries, 1997). Thus, at Mt Tom Price mine, once the AMD risk has been determined (or the distribution and character of MCS) the

following principles of the Spontaneous Combustion and Acid Rock Management Plan have been developed for procedure (RTIO, 2010):

- Minimizing the exposure and mining of black shale to the extent possible
- Identification and special handling of black shale that must be mined
- Encapsulation of black shale inside inert waste rock dumps to limit water contact and allow the dumps to be revegetated
- Containment of black shale below the water table in backfilled open pits to limit oxygen contact

Mineral Waste Management teams have been formed to facilitate the implementation of site management.

2.3.2 Treatment of AMD

Both active and passive treatment systems are known to be effective in relation to improving AMD water quality. Passive treatment systems are generally low maintenance wetlands (usually at abandoned AMD sites), which use biogeochemical processes to reduce water acidity and metal loads (Kitto, 2009). However, Mt Tom Price mine practices an active treatment program.

AMD generated from the SEP is pumped to the SSIX pit for storage, which is then pumped to a 2.5 ML buffer tank (30 m up the hydraulic gradient from the AWTP), before it flows weekly to the AWTP for neutralisation (Earth Systems, 2006).

Figure 2.4 The 2.5 ML buffer tank above SSIX pit source, which is then transferred via pipes down the hydraulic gradient to the AWTP (April 2012, Mt Tom Price mine, WA).

However, it should be noted that AMD is not specifically extracted from all pumped water from the SEP and therefore an additional presence of non-acidic water (groundwater) is also being pumped from SEP to SSIX and the AWTP. There is potential to remove this excess pumping of non-acidic water and reduce the overall water volume that the AWTP receives.

The AWTP is a typical low density sludge neutralisation plant consisting of two reactor tanks that operate by added powered hydrated lime (calcium hydroxide, $Ca(OH)_2$) from on site silos. This process raises solution pH to ~9 and precipitates soluble heavy metal ions. Following this, treatment water and precipitates are sent to the tailings thickener feed launder, where it is diluted with coarse tailings from the process plant. Once the tailings and treated sludge continue to the tailings thickener, treated water is decanted off and used for process plant supply and dust suppression (Buller, 2011), as illustrated by Figure 2.5.

Table 2.1 provides a comparison of the typical water chemistry of the influent and theoretical effluent of the AWTP (Earth Systems, 2006)

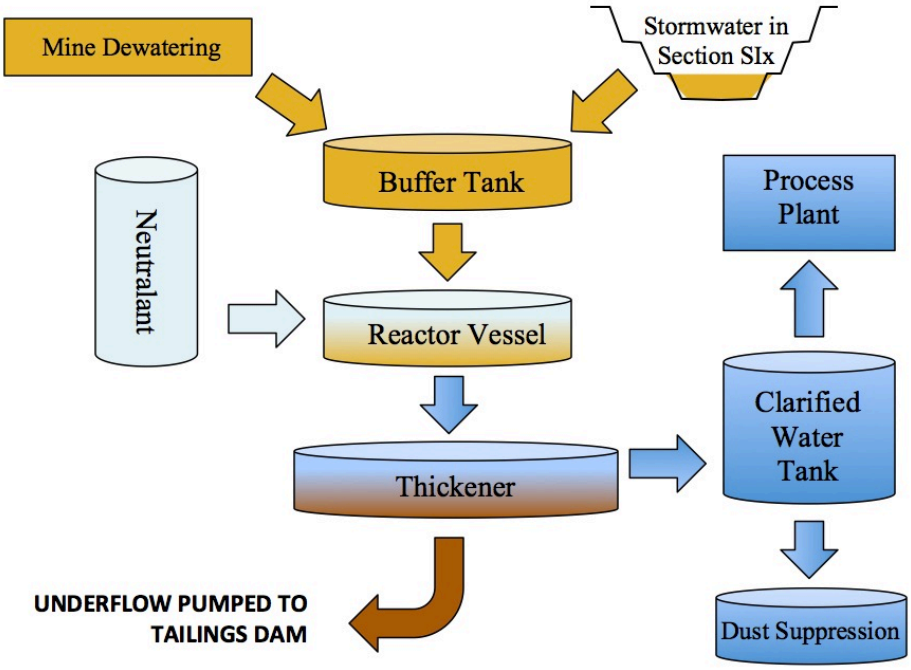


Figure 2.5 Schematic diagram of process flows of AMD treatment through the Mt Tom Price mine AWTP (redrawn from RTIO internal memo).

Parameter	Unit	Influent water (average)	Effluent water (filtered)
pH	-	2.5-3.0	8.5-9.0
Electrical conductivity (EC)	µS/cm	1,500-2,000	≤1,500
Total suspended solids (TSS)	mg/L	350-400	n/a
Acidity	mg/L $CaCO_3$	500-700	0
Alkalinity	mg/L $CaCO_3$	<5	10-300
Sulphate (SO_4)*	mg/L	1,300-1,400	1,000-1,400
Iron (Fe)*	mg/L	60-80	<0.1
Aluminium (Al)*	mg/L	30-40	<0.5
Manganese (Mn)*	mg/L	5-10	<5#
Copper (Cu)*	mg/L	0.5-1.0	<0.1
Zinc (Zn)*	mg/L	1.0-1.5	<0.1
Nickel (Ni)*	mg/L	0.5-1.0	<0.1
Arsenic (As)*	mg/L	0.01	<0.01
Cadmium (Cd)*	mg/L	0.001	<0.001
Cobalt (Co)*	mg/L	0.6	<0.1
Chromium (Cr)*	mg/L	0.05	<0.05
Lead (Pb)*	mg/L	0.001	<0.001
Mercury (Hg)*	mg/L	0.00009	<0.0001
Selenium (Se)*	mg/L	<0.01	<0.01

* Refers to dissolved concentrations rather than total concentrations.

Manganese can be lowered to <1 mg/L with a target treatment pH of 9.0-9.5.

Table 2.1. Comparison of typical water chemistry of the influent and theoretical effluent of the Mt Tom Price mine AWTP (Earth Systems, 2006)

2.4 Geochemical analysis

The geochemical analysis of water involves determining the type and amount of substances dissolved in the water (Fetter, 1994). This is an important method to compare the characteristics of the true composition of different water bodies. The geochemical properties of water are, in the most part, as important as the physical properties and available quantity. Most inorganic solids will dissociate in a water solution, causing the structure to break into a balance of positively charged cations and negatively charged anions. Therefore water analyses will be reported as actual cations and anions that are present. However there are some important exceptions, such as with the element nitrogen, which may occur in several different chemical compounds and polyatomic ions. To clarify commercial labs such as SGS will measure NO_2 concentrations and then from that calculate NO_3^-. In other cases with SGS, if the actual form in solution is unknown then it may be reported in terms of the total concentration of the element, e.g. NO_3 as N.

Certain properties other than the ion components of water are commonly included in water analyses as well. These include properties such as pH, acidity, conductivity (EC), total dissolved solids (TDS) and chemical oxygen demand (COD). Due to the important relevance of pH and acidity to this project, it will be discussed separately in Section 2.5.

2.4.1 Major ions & chemical properties

The following section briefly describes some of the factors that determine the concentrations of aqueous ionic species that are commonly found in the Mt Tom Price AMD from SEP and SSIX, as well as some major ions of the surrounding natural groundwater that may influence the situation. Physical characteristics that affect water chemistry are also mentioned.

The distribution of elements into different forms is termed 'speciation' of the element, which can be affected by environmental conditions such as pH, redox potential, alkalinity and the presence of organic or inorganic compounds (Spitz and Trudinger, 2009). Some specific speciation of metals present in water samples for this project will be explored in further chapters.

These water quality parameters listed are not all necessarily directly related to the formation of AMD, but are useful identifiers when correlating and comparing changes in water quality/geochemistry over time.

Attention should be paid to metals such as iron, aluminium, manganese, copper and zinc, which may be specifically released into waterways due to acidic conditions (Green et al., 2006).

2.4.2 Ions related to AMD composition

Aluminium (Al^{3+}) is the third most abundant element in the earth's outer crust, occurring in substantial amounts in many silicate igneous rock minerals (e.g as feldspars, micas and many amphiboles). However, aluminium rarely occurs in solution in natural water in concentrations greater than a few tenths or hundredths of a milligram per litre (mg/l). The exception lies with water of a very low pH, where the cation predominates and aluminium may be precipitated as an aluminium hydroxy-sulphate (Hem, 1985).

Cobalt (Co^{2+}) is often associated with silver, nickel, lead, copper and iron sulphide ores. The concentration of Cobalt in surface and groundwater (in the U.S) is generally between 1 and 10 µg/kg in populated areas, but can reach hundreds or thousands times higher in areas near mining (Moore, 2005). Simultaneous precipitation or adsorption of cobalt by oxides of

manganese and iron appears to be an important factor in controlling the amounts that can occur in solution in natural water (Hem, 1985).

Copper (Cu^{2+}) occurs naturally as sulphides, sulphates, sulphosalts, carbonate, and as native metal (Moore, 2005). Copper forms rather stable sulphide minerals, with some of the common ore mineral species also containing iron. Copper can commonly be present in concentrations as great as a few hundred mg/L in AMD, once the acidity of such solutions is neutralised the copper is mostly precipitated (Hem, 1985). Copper can also be toxic to aquatic life at very low concentrations (e.g. 1 μM ; Baptista and Vasconcelos, 2006), this will be discussed in later chapters.

Iron (Fe^{2+}) is the second most abundant metallic element in the earth's outer crust, with relatively high content in igneous rock minerals such as the pyroxenes, amphiboles, biotite and magnetite. However, its presence in water is greatly dependant on the oxidation intensity in the system in which it occurs (pH is a strong influence). If present in water in excessive amounts it will form red oxyhydroxide precipitates. Ferric iron can occur in acid solutions as Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$ and in polymeric hydroxide forms. Bacteria oxidise Fe^{2+} to Fe^{3+} in solution (thereby regenerating the Fe^{3+} required for the chemical oxidation of pyrite), acting as an important catalyst during the precipitation of iron and increasing the rate of oxidation reactions (Equation 2-2). However, some misconceptions blame all high concentrations of iron in water on activities of bacteria, which in turn are not resolved by the removal of bacterial species (Hem, 1985).

Manganese (Mn^{2+}) is widely distributed in rocks and soils, with many igneous and metamorphic minerals containing divalent manganese as a minor constituent. The most important sources of manganese occur as oxides, with three possible oxide states (2^+, 3^+ and 4^+). Mn^{2+} predominates in most situations and when released to aqueous solution during weathering the chemistry is somewhat like that of iron in that both metals participate in redox processes, however manganese is somewhat more stable in these processes compared to ferrous iron (Hem, 1985). Manganese is often present to the extent of more than 1 mg/L in AMD and usually persists downstream further than ferric hydroxide. Manganese is known as an essential element in plant metabolism and is noted to accumulate in aquatic plants. Removal of manganese from water by microbial activity has been identified in a study by (Green et al., 2008), where by microorganisms catalyse the reaction of dissolved oxygen with manganese. Magnesium oxides were found on iron bacterium, green algae, cyanobacteria, fungi, protozoans and macrophytes at acid drainage sites in this study. This relationship

between magnesium and aquatic organisms thus potentially increases its circulation in natural water by continuing to be available for solution after plant decomposition (Hem, 1985).

Nickel (Ni^{2+}) is widespread in the environment in igneous rocks such as serpentines (Moore, 2005). Nickel may also substitute for iron in ferromagnesium igneous-rock minerals and tend to be co-precipitated with iron oxides and especially with manganese oxides. The aqueous chemistry of nickel is primarily concerned with the Ni^{2+} oxidation state (Hem, 1985).

Sulphate (SO_4^{2-}) is the most oxidised anionic form of sulphur. The chemical behaviour of sulphur is strongly influenced by the redox properties of an aqueous system. These redox processes, that involve sulphur species, are inclined to be slow unless mediated by microorganisms. The reduced sulphur ion (S^{2-}) forms metallic sulphides of low solubility with most metals and is widely distributed in both igneous and sedimentary rocks. When sulphide minerals, such as the metallic sulphides mentioned above, undergo weathering in contact with aerated water, the sulphur is oxidised to yield sulphate ions that go into solution in the water. Hydrogen ions are produced in considerable quantity in this oxidation process. Sulphate is itself a complex ion, but it displays a strong tendency to form further complex species. The most important of these in natural water chemistry are of the type $NaSO_4^-$ and $CaSO_4^0$ (Hem, 1985).

Zinc (Zn^{2+}) has about the same abundance in crustal rocks as copper or nickel and is thus fairly common. However, zinc has only one significant oxidation state (Zn^{2+}) and tends to be substantially more soluble in most types of natural water than copper or nickel (Hem, 1985). Zinc is mostly obtained from sulphide deposits or their weathering products. Therefore mining is a major release of Zn to the environment, with the levels of dissolved zinc in water increasing as the acidity of water increases (Moore, 2005). Zinc can be an undesirable contaminant for some species of aquatic life (Hem, 1985).

2.4.3 Ions related to surrounding groundwater and natural surface water composition

Calcium (Ca^{2+}) is the most abundant of the alkaline earth metals. Calcium is an essential component of igneous rocks, being dominant in chain silicates pyroxene, amphibole and feldspars, as well as other silicate minerals that are produced in metamorphism. Therefore, it would be expected that high concentrations of calcium be in waters in contact with igneous and metamorphic bodies. However, the slow rate of decomposition of most igneous minerals means calcium concentrations in water are generally low in this case. Presence of calcium in

sedimentary rocks as carbonates (e.g. calcite, aragonite and dolomite) provide a much faster dissolution/precipitation of carbonate minerals, resulting in calcium being a major component of the solutes in most natural water (Hem, 1985). During the neutralisation and buffering processes mentioned in 2.2.2, the potential increased release of Ca into water from $CaCO_3$ can be an early indication of AMD, even before changes in pH are observed.

Chloride (Cl^-) has a geochemical behaviour which reflects the volatility of the element and the fact that compounds of chlorine, with common metallic elements, alkali metals, and alkaline earth metals are readily soluble in water (Hem, 1985). For this reason chloride is commonly used as a reference ion in major ion analysis. Chloride has lower concentrations in many rock types than other major constituents of natural water, however in arid regions in can dominate due to cyclic wetting and drying. During a dry period continuous evaporation occurs until all the solutes have precipitated, followed by partial re-solution of the solutes during a wet season. This allows very soluble minerals (such as sodium salts – NaCl) to dissolve rapidly, compared to less soluble salts (such as gypsum). The end result of the evaporation solution cycle is that the water contains more ions that precipitate only as highly soluble salts. The chemistry left by the cycle results in the effective use of chloride as a reference ion (Hedley, 2009).

Potassium (K^+) is abundant in sedimentary rocks and slightly less common in igneous rocks. Potassium is commonly present in sediments, such as unaltered feldspar, mica particles, illite or other clay minerals. Potassium does not readily disassociate from silicate minerals and exhibits a strong tendency to be reincorporated into solid weathering products. Thus, potassium rarely occurs at high concentrations in natural water, but can become available from decomposed plants, which have assimilated the ions (Hem, 1985).

Magnesium (Mg^{2+}) is an alkaline-earth metal and has only one oxidation state of significance in water chemistry, Mg^{2+}. Magnesium occurs as a major constituent in igneous rocks, various mineral species in metamorphic rocks and many forms in sedimentary rocks (Hem, 1985). In some aspects of water chemistry, calcium and magnesium are considered to have similar effects by their contributions to water hardness. However the geochemical behaviour is very different to that of calcium, with magnesium ions being smaller proving a much higher hydration tendency (Hem, 1985).

Sodium (Na^+) Sodium is the most abundant member of the alkali-metal group of the periodic table, being slightly more abundant in igneous rocks than sediments. When sodium is brought

into solution it tends to remain in that status, causing high sodium concentrations before any precipitate is formed. Sodium concentrations can have a very wide range of concentrations in natural waters, from 1 mg/L in dilute stream runoff to 100,000 mg/L in brines. However, sodium does have the ability to precipitate and can be retained onto mineral surfaces with high cation-exchange capacities such as clays. In dilute waters, where dissolved solid concentrations are below 1000 mg/L, sodium is generally in the form of the Na^+ ion. However in more concentrated solutions sodium attains complex ions and ion pairs such as $NaCO_3^-$ and $NaSO_4^-$ (Hem, 1985).

Silica (SiO_2) is the widely used term when referring to silicon in natural water, but it should be understood that the actual form is hydrated and is more accurately represented as H_4SiO_4 or $Si(OH)_4$. The SiO_4^{4-} tetrahedron is a fundamental component of most of the minerals making up igneous and metamorphic rocks and is present in some form in most other rocks and soils, as well as in natural water. Crystalline SiO_2 as quartz is one of the most resistant to attack by water and a major component of many igneous rocks and the bulk of grains in most sandstones. It seems probable, however, that most of the dissolved silica observed in natural water results originally from the chemical breakdown of silicate minerals by weathering (Hem, 1985).

Nitrate Nitrogen (NO_3^-) is the term used to refer to the nitrogen present that is combined in the nitrate ion. Chemical and biological processes that transfer nitrogen to and from the lithosphere, atmosphere, hydrosphere, and biosphere represent the nitrogen cycle. Nitrogen oxides in the atmosphere undergo various chemical alterations that produce H^+ and finally leave the nitrogen as nitrate. These processes can lower the pH of precipitation in the same way sulphur oxides do (Hem, 1985). Nitrogen can occur in many forms, anionic species such as Nitrate are highly soluble in water allowing stability over a considerable range of conditions and to be readily transported in surface and groundwater. See Section 2.7.1 in relation to the importance of nitrogen for algal growth, alongside phosphorus.

2.4.4 Chemically related properties of water analysis

Conductivity (EC), measured in Siemens per unit length, is the reciprocal of electrical resistivity. The more ions a solution contains the higher its conductivity and hence the lower the resistivity. Table 2.2 shows the common ranges of conductivity for different types of water bodies.

Table 2.2 Ranges of conductivity in difference water bodies (μ S/cm; Hem, 1985)

Water body	EC
Surface and Groundwater	50 – 50,000 μ S/cm
Seawater	50,000 μ S/cm
Brines	225,000-500,000 μ S/cm

EC has the potential to be converted to salinity, however the proportions of different ions contributing to the conductivity need to be known (Drever, 1988).

Total Dissolved Solids (TDS) represents the total amount of solids (mg/L) remaining when a water sample is evaporated to dryness. In principle, it is the sum of all dissolved constituents in a water body/sample.

Salinity means essentially the same as TDS. Table 2.3 shows the common ranges of salinity for different water bodies:

Table 2.3 Ranges of TDS across different water bodies (mg/L; Drever, 1988)

Water body type	TDS
Freshwaters	<1000 mg/L
Brackish waters	1000 – 20,000 mg/L
Saline waters	≥ 35,000 mg/L
Brines	> 35,000 mg/L
Seawater	35,000 mg/L

Chemical Oxygen Demand (COD) is the common way to approximate the total concentration of organic matter (both reactive and non-biodegradable) in water. COD is measured by the amount of strong chemical oxidiser consumed when oxidising the organic matter in the water (Drever, 1988). COD can be produced more reproducibly and more conveniently than **biological oxygen demand** (BOD). BOD is measured by diluting the sample with oxygenated water and measuring the amount of oxygen that has been consumed after a 5 day incubation at 20°C (Drever, 1988). Moderately contaminated streams have a BOD value between 1 and 8 (Nemerow, 1974).

2.5 Acidity

Acidity (as $CaCO_3$) can be described as the amount of base required to raise the pH of a solution to the bicarbonate end point (Drever, 1988). Acidity of waters can be calculated from water chemistry as well as measured directly by titration (Totsche et al., 2006).

Any base-neutralising entities such as protons, metal species, inorganic acids and organic acids (such as humic and fulvic acids) will contribute to the acidity (Green et al., 2006). For example as seen below, in Equation 2-6, acidity (H^+) is released when aluminium precipitates from solution (Refer to Equation 2-4 similarly for iron precipitate; Section 2.2.1).

Equation 2-6 $$Al^{3+}_{(aq)} + 3H_2O = Al(OH)_3 + 3H^+_{(aq)}$$

2.5.1 pH and protonic acidity

pH and protonic acidity account for the concentration of H^+ ions in solution. The pH scale has been defined by the negative logarithm of the H^+ concentration (mol/L), because H^+ concentrations in aqueous solutions are frequently very small and inconvenient to work with.

Equation 2-7 $$pH = -log\,[H^+]$$

2.5.2 Organic acids

Organic acids, particularly humic and fulvic acids, are generally produced by the decomposition of organic matter. Therefore, organic acids enter natural water-bodies most commonly by leachate from soils. These acids contribute protons to soil solution and decrease the pH. Low-pH lakes with a principle solute of organic acid (mostly fulvic) are commonly associated with peat swamps. About half the dissolved organic carbon in rivers and lakes accounts for fulvic and humic acids (Drever, 1988). Rainfall also contains a variety of organic acids (notably formic and acetic), however it decomposes rapidly unless a sample is immediately preserved (Drever, 1988).

There have been instances with a number of plant species where a metal resistance mechanism causes the plant to secrete organic acids (Prasad and Hagemeyer, 1999). For example, aluminium stress in buckwheat (*Fagopyrum esculentum*) caused secretion of oxalic acid into the root soil, which then formed a detoxified Al-oxalate complex that was taken up by roots and translocated into the leaves (Prasad and Hagemeyer, 1999).

High turnover of organic acids, viz. phylate, malate, citrate, oxalate, succinate, aconitate, α-ketoglutarate and malonic has been reported as a mechanism of metal resistance by plants (Prasad and Hagemeyer, 1999).

This identity of the key contributors to acidity is important, particularly with regard to the transport of acid away from the site at which it is generated. Carbonate acidity may be lost to the atmosphere, while acidic metal species may be subject to removal as a result of redox, hydrolysis and precipitation processes. Organic acid mobility may be constrained by adsorption to mineral substrates along flow paths. Proton acidity may be removed by a wide array of both acid-base reactions (Green et al., 2006).

With all these different paths and types of acidity in an aquatic system it is important to be able to measure acidity concentrations.

2.5.3 Total acidity and Calculated acidity

This thesis refers to two terms of acidity, total and calculated, both of which equate the amount of acidity as a concentration of $CaCO_3$ (mg/L). Therefore each acidity measurement is comparable, despite the differing methods of equation. A brief description of each term of acidity is provided here, however the proper method and equation is defined in Section 3.5.

Total acidity of a solution is determined in this thesis by use of titration to first equate the amount of base required to neutralise a solution to an endpoint (usually a pH 8.3). This titratable acidity measurement is then used, along with other relevant information (Section 3.5) to calculate total acidity.

Calculated acidity can be defined by an equation that uses pH and the concentrations of at least three major ions (aluminium, iron and manganese). This equates the amount of potential acidity to be released when the metal ions precipitate and produce H^+ ions during neutralisation.

2.6 Titrations

Acid mine waters have low pH-values (pH 2-4) and typically high concentrations of sulphate, iron and non-ferrous metals, which serve as buffering systems. To understand the acidity and buffering of AMD, acid titrations are commonly used. By this method, a known concentration of base titrant (usually NaOH) is slowly added to the acidic AMD sample until an endpoint pH (usually 8.3) is reached. By then using the known volumes of each solution

(the titrant and titrand) the acidity (as $CaCO_3$ mg/L) of the AMD sample can be calculated. Automated titrators can be used for very precise titrations; from measuring the dispensed titrant volume the acidity is calculated. However, with the same technique titrations can also be done manually using a burette (for accurate readings of titrant used) and a pH meter to record changes in pH.

Titrations are not only used to determine endpoints, but they also hold additional information about the buffering systems in the water sample.

The understanding of buffering systems of acidic waters, along with the pH and acidity, have special importance for, (1) the evaluation and optimisation of AMD treatment options; (2) environmental studies, because important issues such as mineral solubility, metal toxicity and nutrient availability are governed by these factors, and (3) water quality forecasts (Totsche et al., 2006).

2.6.1 Titration curves

Titration curves are produced by recording the pH changes of a solution, during the incremental addition of a known volume and concentration of titrant. The curve produced makes an ideal tool for characterisation of acidic chemical species in AMD, with high precision and reproducibility.

Figure 2.6 shows an acidity titration curve example (Totsche et al., 2006) and how acidic species can be identified. In this example the titration curve is split into its different buffering components, showing at what stage each acidic species individually influences the titration by buffering out and eventually precipitating (the opposite process of what has previously been discussed in Section 2.2.3 and Figure 2.3).

Buffers are a combination of weak acids and their conjugate bases. Weak acids have the ability to partly dissociate in water and cause the pH value to remain constant at a certain range and plateau, by reaction with the base. By addition of base the pH will remain moreover constant as long as there is enough buffer present. When the whole buffer is used up, the buffering capacity is exhausted and the pH-value will rise with respect to the addition of base.

Titration curves are also very useful for illustration of the changes of geochemical characteristics in a water body over time.

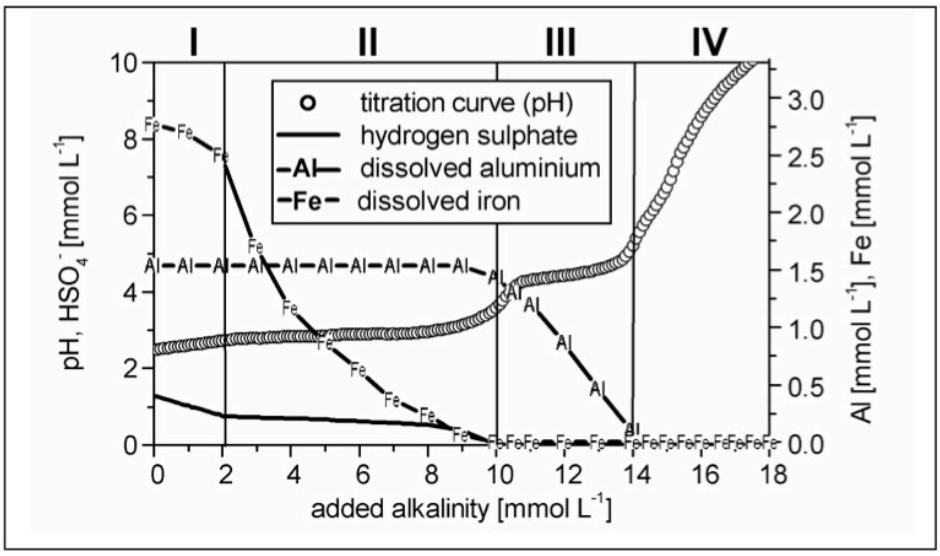


Figure 2.6. An acidity titration example split into its different buffering components, showing at which range each acidic species individually affects the titration curve and buffers out (Totsche et al., 2006).

2.6.2 Hot titration

For water samples that contain hydrolysable metal ions (or reduced forms of polyvalent cations), such as AMD or other industrial wastes, it is recommended to use the hot peroxide titration treatment (hot titration). This is in accordance with the American Public Health Association methods for the analysis of acidic waters (APHA, 1998). This form of titration uses the addition of hydrogen peroxide (H_2S_2) and subsequent boiling of the sample to completely oxidise any remaining metals in the solution, in order to measure all the acidity produced during precipitation of metals during titration.

This reaction will only work with samples of a pH below 4; therefore a sulphuric acid solution can also be added to those that require a lower pH before the addition of the H_2S_2. This method also measures some organic acidity (Green et al., 2006).

This hot titration method incorporates all potential oxidisable, hydrolysable metals and typically exhibits close correspondence with calculated acidity values by the summation of all key contributing species, which could potentially produce acid when precipitating out of solution. Traditional titration methods (referred to from here on as cold titrations) often suffer imprecise end-points as a result of the continuing oxidation of some metals, the following

points show that carbon dioxide (carbonic acid in solution) can also be accountable for much of this:

- As mentioned in Section 2.2.3 there is a presence of carbonates in solution (due to buffering activities). When these carbonates precipitate out during a titration CO_2 is released, which can alter the acidity of the titrand and cause drifting in the pH record. However, if preparing a hot titration, the CO_2 is released during boiling (Green et al., 2006).
- Atmospheric CO_2 (and other dissolved gasses) may have also contributed to the initial acidity during sampling and may be lost from shaking a sample during storage thus releasing gases when opening sample for titration, or if a titration is not promptly completed after the opening of a sample (APHA, 1998).
- During the mixing or swirling of a titration flask atmospheric CO_2 can dissolve into solution and affect the endpoint measurement (Totsche et al., 2006).

It can be important to complete both a cold and hot titration for comparison and understanding of metals and acidic species present in the water sample.

Figure 2.7 shows a hot and cold titration comparison from Green's (2006) study. This acknowledges the initial lower pH of the hot titration sample, as a result of additional acidity from the oxidation of the sample. The hot titration sample displays a larger consumption of added titrant (base) in the first half of the equation due to the readily hydrolysable metals, which underwent oxidation, to attain the added base more quickly. The cold titration thus shows larger titrant consumption in the second half of the equation due to the delayed oxidation of metals (such as Mn) as the titration progresses and ions hydrolyse and precipitate (Green et al., 2006). From Greens study hot and cold titration comparisons typically showed these same results of cold and hot acidity being equal at around pH 5.5 and thus below this pH value hot acidity dominates, above this pH value cold acidity dominates (Green et al., 2006).

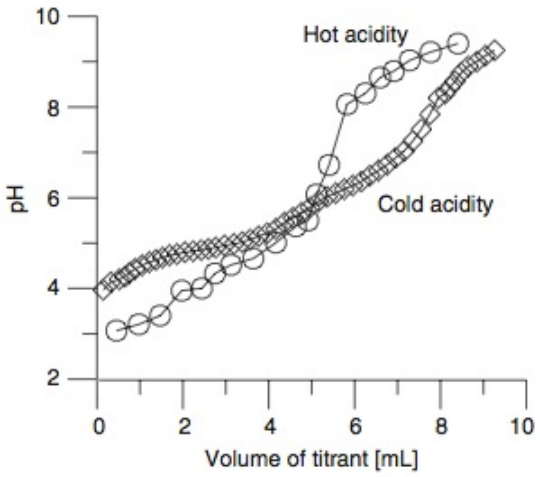


Figure 2.7 Example of the differences in titration curves of hot and cold acidity titrations (Green et al., 2006)

2.7 Algae in Acidic environments

To understand all elements that affect the acidity of waters at Mt Tom Price mine, the algal growth (that has been detected in the 2007 investigation of the SSIX pit) must be investigated for its potential to provide organic acidity. Often in low numbers algae are not usually a problem and can be an essential part of a healthy body of water (as they produce oxygen). Some types of algae can complete nitrogen fixation, which improves the fertility of the water body and increases primary production (See Section 2.7.2; Green, 2008)

Algal growth in acidic environments is not a common occurrence; AMD can have adverse affects on the distribution and abundance of freshwater organisms typically including algae in most cases. Yet it is rare to find even the most inhospitable polluted areas entirely devoid of biological life. AMD environments commonly contain an abundance of microorganisms such as bacteria, archaea, fungi and protozoa (Lottermoser, 2010).

There are occurrences where a low frequency of individuals, with a genetic variability, can tolerate pollutants and therefore be the only 'survivors' when pollution levels rise (Begon et al., 2005). They may then become the founders of a tolerant population. Figure 2.8 shows an example of this from a study on isopod populations with response to exposure to metals. The study displays how metal tolerant species can build a strong population throughout winter and summer climates, despite lack of genetic diversity, in comparison to non-polluted environments (Begon et al., 2005; Ross et al., 2002).

There are some plants which are hyper-accumulators of heavy metals and not only tolerate the pollutants but can also effectively accumulate concentrations of pollutants, thus potentially being able to play a vital role in bioremediation (Begon et al., 2005). The Cyanobacteria, *Synechoccus* can display hyper-accumulation due to a special outer membrane protein layer it possesses, which is highly interactive with metal ions (such as Ca^{+}; Brooks, 1998).

Hyper-accumulators support bioremediation options to rehabilitate retired mining areas through passive treatment by a constructed wetland. Passive treatment systems (as mentioned in Section 2.3.2) are generally low maintenance systems, which use biogeochemical processes to reduce water acidity and metal loads (Kitto, 2009). These wetlands have abundant clay, organic matter, algae, bacteria, fungi and lichens, which are effective in removing dissolved contaminant concentrations (Lottermoser, 2010). It is unknown at this stage whether the algal growths identified in the SSIX pit have the ability of hyper-accumulation.

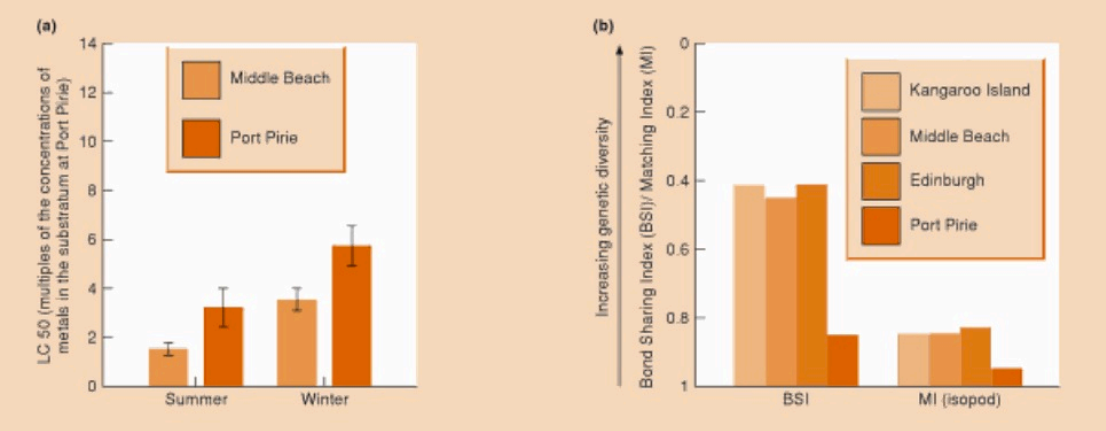


Figure 2.8. The response of the marine isopod to pollution around a lead smelting operation (Port Pirie). (a) Tolerance, from both summer and winter was significantly higher ($P < 0.05$) at Port Pirie than for animals from an unpolluted site (Middle beach). (b) Genetic diversity was significantly lower at Port Pirie than at three unpolluted sites (Begon et al., 2005).

2.7.1 Algal growth in SSIX pit

It is important to understand the species that are present in an algae bloom. This can be done by the use of laboratory algae counts to confirm the nature of the algae (Green, 2008). In 2007 two different types of phytoplankton (microscopic algae) were identified in the Mt Tom Price mine SSIX pit.

The first, classified in the *Chlorophyceae* class of the green algae and from the phylum Chlorophyte. This coccoid (oval shaped) unicellular algae is primarily found in freshwater and exhibits an even number of flagella, which assist in movement (Roy et al., 2011). These flagellates can be described as well adapted to the existing acidic conditions in the SSIX pit, because they have the ability to migrate to convenient places rich in nutrients and to overcome local chemical limitations (Beulker et al., 2003).

In comparison, the second phytoplankton was classified a non-flagellate blue-green algae in the *Synechocystis* genus, a Cyanobacteria. Figure 2.9 shows an example of this identification.

Green (2008) documented how cyanobacteria blooms can dominate a water body due to the following conditions, which could also generally describe the beneficial conditions for most algal blooms:

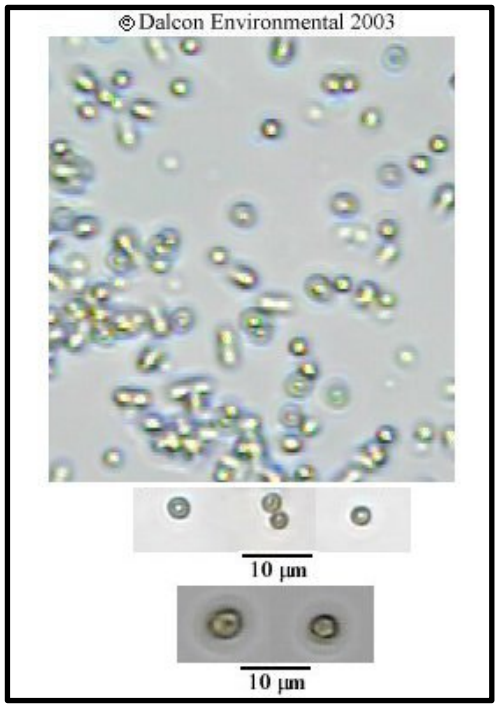
- Nutrient levels, particularly phosphorous and nitrogen, are sufficient to support growth.
- Water is still or turbulence is minimal
- Weather pattern is stable for a long time
- Weather is warm (although blooms can occur in cooler weather too)

Additionally as would be expected, both types of phytoplankton are mesophilic with optimum growth between temperatures 25 °C and 40 °C. Below or above these temperatures cause stress to cells.

Green (2008) also documented how cyanobacteria can be visually observed in a water body by the following characteristics if:

- The water is discoloured so the surface looks like green acrylic paint.
- There is an unpleasant odour.
- Surface scums, which are vulnerable to wind effects, may appear at different places on the water body at different times. The blue-green algae may disappear and reappear on subsequent days, or accumulate on the downwind edges of the water holding facility.

Figure 2.9. Microscope identification of the genus *Synechocystis* (Dalcon Environmental commercial lab, Perth, WA).



2.7.2 Iron reducing bacteria

Iron reducing bacteria (IRB) has also been known present in the SSIX pit during phytoplankton blooms. Precisely, as <20 CFU/mL during the 2007 algal bloom in the SSIX pit (from archived RTIO chemical reports). IRB accelerate the conversion of ferrous iron to ferric iron, which subsequently produces an insoluble iron oxy-hydroxide (RTIO, 2013). The iron oxy-hydroxide has a strong adsorption capacity for cations and may also attract other solids (precipitates) once formed, which can cause blockage of pipes and pumps of dewatering bores. In low flow environments IRB can also form sticky gelatinous substances, which can attached and block pumps and pipes as well (RTIO, 2013). This is known as biofouling. It is likely the iron reducing characteristics are unrelated to phytoplankton presence, rather that an increase in biological activity is noted in the pit water overall. Phytoplankton blooms could therefore be an indication for the issues that can result from IRB presence.

2.7.3 Nutrient limitations of algal growth

The nutrient level status in a water body can often be limited by nitrogen and Phosphorous (Taylor et al., 2007). Some cyanobacteria can undertake nitrogen fixation by converting atmospheric nitrogen (N_2) to ammonia (NH_3). Thus allowing the uptake of ammonia into amino acids and other organic molecules of the cyanobacteria, promoting further growth. Nitrogen fixing cyanobacteria are some of the most self sufficient organisms, due to the ability for their growth with only light, CO_2, N_2, water and some minerals (Taylor et al., 2007).

However, in some cases N_2 is only slightly water-soluble and therefore the highly mobile presence of nitrate in an aquatic system (due to its in-absorbency to other solids) is more useful for the addition of useable nitrogen to the aquatic system (Green, 2008). Bacteria can reduce nitrate to NH_3 via the intermediate denitrification stages of NO_2^-, NO and N_2O. The bacteria require soluble organic carbon energy to perform denitrification. The process then becomes proportional to the temperature and the bacteria concentration. (Green, 2008).

Taylor et al. (2007) documented a series of nutrient enrichment experiments (completed in the Sargasso Sea), which proved that iron also acts as a limiting nutrient for primary production. It was found that adding iron stimulates the growth of nitrogen fixing cyanobacteria. The extra nitrogen, which is then added to the water body, further stimulates primary production and phytoplankton growth.

Due to the fact that even if large concentrations of nitrogen are not in the water it is possible for algae and bacteria to fix nitrogen from the atmosphere, the control of phosphorus concentrations is often regarded as the best means of controlling aquatic productivity (Green, 2008).

2.7.4 Removal of algae and/or microbial activity and organic acidity

Removal techniques will be acknowledged briefly here, just to be kept in mind during results analysis, these ideas will be more thoroughly revisited later in the discussion chapters.

One strategy to prevent AMD is through the use of biocides to inhibit the bacteria responsible for causing AMD (such as *A. ferrooxidans*). Anionic surfactants are bacteriocidal at low pH values and have been used to inhibit acidophilic Fe- and S-oxidising bacteria (Jambor et al., 2003). If this same bacterial inhibiter could have an effect on the cyanobacteria, then perhaps

this is an effective method to both reduce effects of AMD and the growth of phytoplankton, which are potentially causing organic acidity.

A second method of algae/phytoplankton removal to briefly acknowledge at this stage is the use of chemical algaecides. Chemical algaecides such as copper sulphate are frequently used to control algae blooms. Studies have shown the effective removal of cyanobacteria with the use of a copper sulphate algaecide, however a species of green algae that was also present (alike the *Chlorophyta* also previously found in SSIX), proved more tolerable to a copper sulphate treatment. Nevertheless, high copper levels (at 5 ppm) resulted in substantial declines in all algal taxonomic groups (Hudnell, 2008) and this technique will be further reviewed for removal of the algae potentially forming organic acidity in SSIX.

3 Sampling and laboratory analysis methods

3.1 Introduction

Geochemical analysis of water samples, acidity titration and algae identification methods were selected to investigate the issues of acidity inconsistency and the potentially related algal growth in the SSIX pit, as discussed in the previous chapter. Therefore, water samples were collected by the Mt Tom Price on-site Environmental Monitor from selected sites of interest.

Site descriptions have been supplied in Chapter One (Section 1.4) for the SEP pit and SSIX pit, where surface water sampling has taken place. Groundwater samples for comparison of water geochemistry were also collected from the SEP bores WB06SEP01 and WB11SEP02 (archived data is collected from a larger range of bores for further comparison). Chapter One describes how the SEP area supplies the source water of the SSIX pit, thus no other surrounding area was included for sampling for this project. These samples are thus event based for the purpose of this project and related to seasonal climatic events

Four different periods of water sampling were undertaken specifically for this project, by the methods described in this chapter. Two sets of samples were taken in February and April (the wet season) and then two more in August and December (the dry season).

This chapter will explain the methods of how these water samples were used for geochemical analysis, biological analysis and acidity titrations to characterise acidity.

Field records for conductivity and pH, during the time of sampling, were the few field tests taken. Other geochemical or physical characteristics were not taken during field sampling for this project. Therefore have not been included in methods. However, there is archived data for water temperatures that will be acknowledged in Chapter 4.

3.2 Environmental monitoring and collection of samples

Water samples are collected regularly at Mt Tom Price mine, from surface and groundwater sites of interest, for routine checking of potential mining effects on water quality. It is

essential for Mt Tom Price Mine to maintain these regular sampling procedures (from specific areas and sites), to continue identification of geochemical changes and assist prevention of negative environmental effects over time.

Water monitoring should ideally be undertaken at least quarterly (four times a year), but in reality this is not always possible and monitoring can also occur as an event based record. For example, water monitoring can occur in relation to a physical observation, a related project at the time or a specific rainfall event. Event sampling is usually reliant on climate, since water flow at many sampling locations at Mt Tom Price mine is dependent upon the occurrence of major rainfall events.

3.2.1 Laboratory analysis and reports

RTIO water samples are collected (by the methods to be mentioned below) and sent currently to the SGS commercial lab in Perth for analysis of geochemical properties (NB. lab suppliers for RTIO can change due to contract negotiations). SGS reports are compiled in the EnviroSys. database by RTIO, which archives data back to 2002. This information is used to construct the RTIO Tom Price Annual Water Quality Report (Staines and Buller, 2012).

This archived data has also been made available for use by this project. The data will be used to equate trends over time in relation to water geochemistry for the specified sites (e.g. SSIX and SEP pits), alongside the four samples collected specifically for the purpose of this project.

NB. SSIX Pit February (2012) samples for this project were sent to Cawthron Laboratory (Nelson, NZ) for water geochemistry analysis. This was for trial purposes and proved to be inconvenient, and so all subsequent samples have been sent to SGS Laboratory. Biological analysis (presented in Section 3.4) were completed by Dalcon Environmental, Perth.

3.2.2 Surface water sampling

Surface water samples were collected for this project from the SSIX pit and the SEP pit (see Section 1.4 for site descriptions). Casey Miller, a RTIO Hydrogeologist, collected the February (2012) samples. Rob Dallosto, the on-site Environmental Monitor, collected all other samples (April, August and December, 2012).

Standard procedures were followed for both periods. The bottles used for water sample storage are provided by SGS commercial lab (Perth), to assist with standardised sampling methods (Figure 3.1).

Bottles are placed into the discharge flow and rinsed 3 times prior to collection of sample. The bottle is then filled as close as possible to the top. The bottle is capped immediately and samples are kept chilled and secure at all times with delivery to destination laboratories within 24 hours of sampling.

Samples that are used for biological oxygen demand (BOD) were stored in a dark coloured bottle.

Point source discharges are sampled as far away as possible from the outlet pipe to ensure representative samples. Figure 3.2 shows the sampling site at SSIX in relation to the outlet pipe, from the SEP source.

Other surface water sample sites (from archived EnviroSys data), are those from the SEP and SSIX bores, the Cyclone tank and SSIX discharge (Section 1.4.3).

Figure 3.1 August water samples from the specified sites for this project, in the standard SGS 1 L sample bottles.

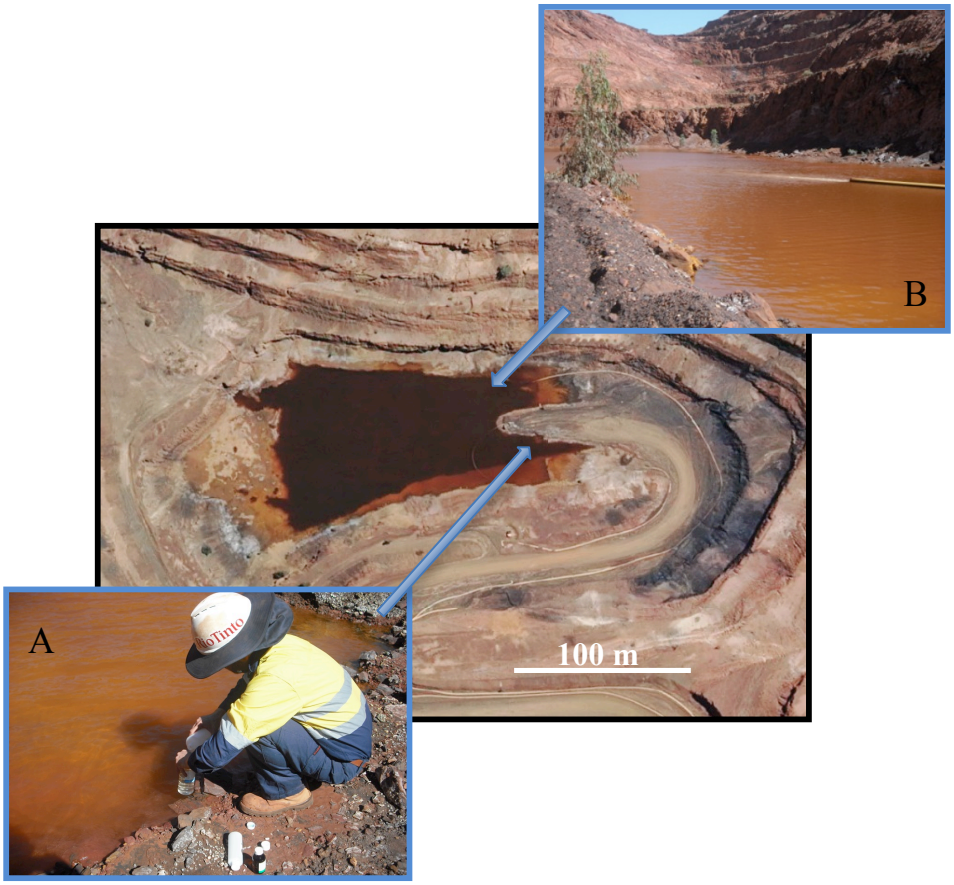


Figure 3.2 (a) Sampling site by Rob Dallosto. (b) Input to SSIX, outlet pipe from SEP. (SSIX, Mt Tom Price Mine, April 2012)

3.2.3 Groundwater sampling

Groundwater samples were collected from SEP bores WB06SEP01 and WB11SEP02. The same sets of samples were collected from both wet and dry seasons as mentioned previously.

Groundwater bores are clearly identified in the field for consistent resampling. Production bores are sampled by allowing the tap to flow for one minute before each sample bottle was rinsed three times and then filled. For sampling from an observation bore, the industry standard is to purge three times the volume of the bore before the sample is taken. After collection, the same procedure is followed as for surface water samples, i.e. the water samples are kept chilled and secure at all times with delivery to destination lab within 24 hours of sampling.

3.3 Geochemical analysis of water samples

This section covers the processes of geochemical analysis of each water sample collected for this project and those that have been archived in the RTIO EnviroSys database. As previously mentioned in Section 3.2.1 water samples are sent to the SGS commercial lab for geochemical analysis reporting (NB. One sample for the SSIX Pit, in February 2012, was sent to Cawthron Labs NZ). SGS has been used by RTIO for the entirety of the geochemical reporting used in this project, which delivers consistency and precision when it comes to providing comparable, reliable data

3.3.1 Data Quality Assurance

Most samples that undergo geochemical analysis by SGS can be applicable for a basic check of accuracy by completing an ion charge-balance, which is displayed at the bottom of an SGS report if requested.

This is based on the principle that an aqueous solution is electrically neutral and the total number of equivalents of cations must equal the total number of equivalents of anions. If this is not the case the balance-charge will produce an error percentage of the total ion concentrations (a recommended limit for accepting a valid analysis is 5%; Hedley, 2009). This was determined with the following equation:

Equation 3-1

$$\boldsymbol{Reaction\ Error} = \left(\frac{[\Sigma_{CATIONS} - \Sigma_{ANIONS}]}{\Sigma_{IONS}}\right) \times 100$$

It is also important to understand the limits of reporting (LOR) which are individual terms for each parameter (shown in Table 3.1), so that there can be a determined value of whether any variation in the data be deemed significant.

The original SGS reports (for the related sites in this project) have also been acquired from 2007 onwards. This data has been used to double check EnviroSys. entries and follow up certain reports.

It is possible to check pH and conductivity laboratory data against field measurements recorded in the Envirosys Database for this project.

3.3.2 Water geochemistry analysis methods

SGS water geochemistry analysis is conducted using standard methods to determine concentrations of various aqueous ions and geochemical properties of the water sample.

It should be noted that over time the LOR (for the reporting of analyses by SGS and in the EnviroSys database) can vary due to changing standard methods. The current method by RTIO, for plotting Envirosys data that may be below the LOR, is to present the point as half the LOR.

Table 3.1 acknowledges the main standard methods that were used by SGS for the water sample analyses presented in this project.

As covered in Chapter 2 (Section 2.5), the water quality parameters listed below (species measured) are not necessarily directly related to the formation of AMD, but are useful identifiers when correlating and comparing changes in water quality/geochemistry over time.

Table 3.1 SGS standard methods for geochemical analysis of water samples, compiled from information from SGS.

Method ID	Species Measured	Units	LOR	Methodology Summary
AN274	Chloride, Cl-	mg/L	1	Chloride by Aquakem Discrete Analyser (DA; this fully automated instrument can conduct multiple geochemistry reactions for water and environmental samples, ensuring continuous and reliable data). Chloride reacts with mercuric thiocyanate forming a mercuric chloride complex. In the presence of ferric iron, highly coloured ferric thiocyanate is formed which is proportional to the chloride concentration. Reference APHA 4500Cl-.
AN275	Sulphate, SO_4^{2-}	mg/L	1	Sulphate by Aquakem DA: Sulphate is precipitated in an acidic medium with barium chloride. The resulting turbidity is measured photometrically at 405 nm and compared with standard calibration

				solutions to determine the sulphate concentration in the sample. Reference APHA 4500-SO_4^2.
AN279/ AN293	Phosphorous, P	mg/L	0.01	The sample is digested with Sulphuric acid, K_2SO_4 and $CuSO_4$. All forms of phosphorus are converted into orthophosphate. The digest is cooled and placed on the discrete analyser for colorimetric analysis.
AN320/ AN321	Dissolved Metals	mg/L	0.001: Cd. 0.005: Cr, Cu, Pb, Mn, Ni. 0.01: Co, Mo, Zn. 0.02: Al, As, Fe, Se, Si. 0.05: Sb, Si (Sol). 0.1: Mg, K. 0.2: Ca. 0.5: Na	Metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-OES): Samples are preserved with 10% nitric acid for a wide range of metals and some non-metals. Solutions are aspirated into an argon plasma at 8000-10000 K (Kelvin) and emit characteristic energy or light as a result of electron transitions through unique energy levels. The emitted light is focused onto a diffraction grating where it is separated into components. Photomultipliers or CCDs are used to measure the light intensity at specific wavelengths. This intensity is directly proportional to concentration. Corrections are required to compensate for spectral overlap between elements. Reference APHA 3120B.
AN101	pH	pH units	0.1	pH in Soil Sludge Sediment and Water: pH is measured electrometrically using a combination electrode (glass plus

				reference electrode) and is calibrated against 3 buffers purchased commercially (pH 4, 7 and 10). Reference APHA 4500-H+
AN106	EC & TDS	µS/cm	2	Conductivity and TDS: Conductivity is measured by conductivity meter with temperature compensation and is calibrated against a standard solution of potassium chloride. Conductivity is generally reported as µmhos/cm or µS/cm at 25°C. Total Dissolved Salts can be estimated from conductivity using a conversion factor, which for natural waters is in the range 0.55 to 0.75. SGS use 0.6. Reference APHA 2520B.
AN114	TSS/VSS	mg/L	5	Total Suspended and Volatile Suspended Solids (TSS/VSS): The sample is homogenised by shaking and a known volume is filtered through a pre-weighted GF/C filter paper and washed well with deionised water. The filter paper is dried and reweighed. The TSS is the residue by the filter per unit volume of sample. Reference APHA 2540 D
AN135	Alkalinity	mg/L	1: CO_3. 5: HCO_3, $CaCO_3$.	Alkalinity (and forms of) by Titration: The sample is titrated with standard acid to pH 8.3 (P titre) and pH 4.5 (T titre) and permanent and/or total alkalinity calculated. The results are expressed as

				equivalents of calcium carbonate or recalculated as bicarbonate, carbonate and hydroxide. Reference APHA 2320. Free and Total Carbon Dioxide may be calculated using alkalinity forms only when the samples TDS is <500mg/L. If TDS is >500mg/L free or total carbon dioxide cannot be reported. Reference: APHA4500CO2 D.
AN140	Acidity	mg $CaCO_3$/L	5	Acidity by Titration: The water sample is titrated with sodium hydroxide to designated pH end point. In a sample containing only carbon dioxide, bicarbonates and carbonates, titration to pH 8.3 at 25°C corresponds to stoichiometric neutralisation of carbonic acid to bicarbonate. Both hot and cold titration measurements are available by SGS. Section 3.5.1 and 3.5.2 (of this thesis) display the personal method chosen for titrations comparable to this SGS method. Reference APHA 2310 B.
AN181	COD	mg/L	10	Analysis of COD by Semi Closed Reflux: The sample is refluxed with strong acid and a known excess of oxidant. After digestion the unreduced oxidant is back titrated to determine the amount of oxidant consumed. The geochemically oxidised matter is calculated in terms of oxygen equivalents.

				Reference APHA 5220 B.
AN190	TOC and DOC	mg/L	1	Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) in Water: A homogenised micro portion of sample is injected into a heated reaction chamber packed with an oxidative catalyst that converts organic carbon to carbon dioxide. The CO_2 is measured using a non-dispersive infrared detector. The process is fully automated in a commercially available analyser. If required a sugar value can be calculated from the TOC result. Reference APHA 5310 B.
AN258	Nitrate	mg/L	0.05	Nitrate and Nitrate by Flow Injection Analysis (FIA): In an acidic medium, nitrate is reduced quantitatively to nitrate by cadmium metal. This nitrate plus any original nitrate is determined as an intense red-pink azo dye at 540 nm following diazotisation with sulphanilamide and subsequent coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. Without the cadmium reduction only the original nitrate is determined. Reference APHA 4500-NO3-F.

3.3.3 Presentation methods and Schoeller diagrams of water geochemistry data

The water geochemistry data, acquired by SGS reports, will be presented as temporal data plots showing trends in major ion concentrations over time (Figure 4.8 – 4.13). In order to

focus on changes in major ion concentrations from a certain period of time, Schoeller diagrams will be used.

Schoeller diagrams are commonly used to show the geochemical composition of multiple samples simultaneously (Hedley, 2009). Multiple data series are plotted for comparison of select geochemical major ion concentrations. This graphing method is commonly used to compare water geochemistry from different locations, with concentrations in meq/L on the 'y' axis and the individual ion on the 'x' axis.

This project uses Schoeller diagrams to compare data over time from one sample location, by identifying changes in water geochemistry using multiple dated data series.

3.4 Biological Analysis of water samples - Phytoplankton count

Water samples were taken to count phytoplankton. This determines the absence/presence and relative abundance of any phytoplankton/algal species in the water sample.

Water sampling is undertaken by the same procedures mentioned earlier (Section 3.2.2) by the onsite Environmental Monitor. The water sample was then couriered to Dalcon Environmental commercial lab in Perth for analysis. In the algal findings, of the SSIX pit, from 2007 the water sample was preserved under Lugols preservative solution, however in 2012 samples are unpreserved (due to recent restrictions on the Lugols preservative at Mt Tom Price Mine) but transported under chilled conditions with delivery 24 hours from sampling.

The phytoplankton count procedure used at Dalcon Environmental is initially dependent on the amount of cells detected. Multiple procedures were undertaken by Dalcon Environmnetal during this project, which can be identified in the individual phytoplankton count reports (Appendix IV). The following presents the four methods utilised during this thesis.

The Sedgewick Rafter Chamber (SRC) Long (44) method is used when a large number of cells are present (Arklie, 2012). This is completed on a raw water sample, which means the sample has not been pre-concentrated or diluted to alter phytoplankton count rate.

The samples are analysed in a Sedgewick Rafter Chamber at 400x magnification. The chamber is a glass slide (50 x 20 mm), 1 mm deep, or area 1,000 mm^2 and holds 1 mL of sample. This type of slide allows for the largest species of phytoplankton to be held, which

makes it best suited for large and relatively scarce organisms, which can be detected at just a few per millilitre (Andersen, 2005). However, many species as small as 10 μm can be also recognised in it (Andersen, 2005). Dalcon Environmental methods allow the sample to settle for approximately 20 minutes before counting, this is very important when cells are small and contained in a relatively deep chamber where movement may occur and disrupt counting. During the SRC Long (44) method, one long transect of the sample is analysed (hence the 44 conversion factor to get a result of cells/mL).

The SRC Camp (9) is a similar process, however it is conversely used when there are fewer cells present. Due to the lower number of cells, 5 long transects are counted for phytoplankton (compared to the 1 transect of the SRC Long (44) method), the conversion factor of 9 is used to obtain cells/mL (Arklie, 2012).

Newer methods that have now been adopted by Dalcon Environmental include the **Raw Count (1)**, which is a complete chamber scan at 200x magnification for any large algae. A transect of 50 squares is then completed at 400x magnification for an picoplankton (Arklie, 2012).

Identification of phytoplankton can also be completed by non-quantitative methods by the use of fluorescence. The **Qualitative Count (1)** is usually used when a phytoplankton count is unachievable, due to a very low or no count result. A concentrated sample is required when very few cells are detected. To do this a 100 mL sample is settled in a graduated cylinder for 48 hours, then the top 90 mL is siphoned off leaving a 10x concentrated sample (Arklie, 2012). Fluorescence is then added to the sample to identify the phytoplankton cells, which then leads to an enumeration using an un-concentrated sample (Arklie, 2012).

Prior to preserving the sample, notes are taken of any colour, scum or odours present (Appendix IV).

3.5 Acidity Titration Analysis

For acidity analysis of the 2012 samples, acidity titrations were completed to investigate the acidity values and titration curve analysis. The acidity titration method that was followed used the APHA 2310B standard method (APHA, 1998).

AMD water samples contain hydrolysable metals (Section 2.1.2), which effect titration results by continued buffering and drifting of the pH. The Hot Titration method

(Section 2.7.6) was completed, to prevent the effect hydrolysable metals cause during a titration, to produce a reliable, consistent titration curve for acid species analysis.

In terms of the unit of concentration, normality (N) is used here for consistency with the standard, rather than molarity (M). Normality is similar to molarity, but rather than a measure of the number of moles per litre it measures equivalents per litre. For acids and bases, an equivalent can be considered as the mass that produces 1 mole of hydrogen or hydroxide ions, respectively (Myers, 2003). Therefore a 1 M solution of H_2SO_4 dissociates into 2 moles of H^+ and 1 mole of SO_4-, thus the solutions normality will be 2 N because 2 moles of H^+ ions are present per litre of solution.

3.5.1 Hot Titration

A 30 mL sample size, of the AMD water sample in question, is chosen for titration. This sample is pipetted into a 250 mL beaker and the initial pH is measured.

If this pH is >4 then 5 mL increments of 0.02 N sulphuric acid (H_2SO_4) are added into solution to reduce the pH to <4. The pH meter is then removed from the sample while 5 drops of 30% hydrogen peroxide (H_2O_2) are added into solution The sample is then boiled in a round bottom flask in a heating coil for 5 minutes, under a fume hood (Figure 3.3).

Once the sample has returned to room temperature, it is then titrated against a suitable concentration of standard alkali NaOH (e.g. 0.01 N), at increments of roughly 0.5 mL, until a pH of 8.3 is passed (Figure 3.4). A magnetic stirrer is constantly in use during the titration to catalyse the reactions. Depending on the type of pH probe a recording is made when a pH reading is stable for over 5 seconds. The pH probe (Mettler Toledo FiveGo) shown in Figure 3.4 had its own stabilised pH symbol that identified the accurately determined pH reading.

Titration curves are then constructed by plotting the observed pH values versus the cumulative volume of NaOH titrant added (mL), and titratable acidity graphs can be used for further acidity characterisations. A target pH of 9-10 was used to extend the curve to aid interpretation and comparison, although the end point target was pH 8.3.

Each water sample had three hot titration replicates conducted, the average result was then chosen by the titration curves and those values used for the acidity calculation. Three Cold Titration replicates were also completed for comparison of averages.

Figure 3.3 Hot Titration pretreatment/apparatus for samples with pH >4. Solutions of 30% H_2O_2 and 0.02 N H_2SO_4 (left) and the heating coil with treated sample in round bottomed flask (right).

3.5.2 Cold Titration

Cold titrations were carried out on each sample to compare the effect of the hydrolysable metals. To carry out a cold titration the same procedure as mentioned above is followed without the pre-treatment of hydrogen peroxide or sulphuric acid.

There is likely to be greater drifting of pH values as the titration progresses towards the end point (pH 8.3), because of the delayed oxidation and higher presence of hydrolysable metals (that have not been hot titration pre-treated) consuming more base. There may also be a large influence of carbon dioxide dissolved in solution disrupting the titration progress, as described in Section 2.6.2.

3.5.3 Total and calculated acidity measurement

Once the titrations are complete and the SGS water geochemistry data has been collected, the total and calculated acidities can be determined (Equation 3-2 and Equation 3-3). These values can be compared to identify the presence of any unknown source of acidity in the total acidity, which has not been accounted for in the calculated acidity.

Total acidity of a solution is determined by first equating the amount of base required for a titration of the solution to an endpoint pH 8.3. The relevant information is then input into the following equation, Equation 3-2.

Equation 3-2

$$\boldsymbol{CaCO_3\ (mg/L) = \frac{V \times N \times 50{,}000}{mL\ sample}}$$

Where:

V is ml of standard titrant used

N is normality of the standard titrant

50,000 is the milligram equivalent weight of $CaCO_3$

Calculated acidity can be defined by the concentrations of at least three major ions (aluminium, iron and manganese). This equates the amount of potential acidity to be released when the metal ions precipitate and produce H^+ ions during titration to an endpoint pH 8.3.

As shown below, the ion concentrations are multiplied by their relative charge and divided by the molar mass. It should be noted that this method assumes the water is oxidised and a presence of ferric iron. The pH of the solution is also used to account for the acidity caused by the additional free H^+ ions in solution. The following equation thus results in milligram equivalent weight of $CaCO_3$ as acidity, or alternatively alkalinity.

Equation 3-3 $$\boldsymbol{CaCO_3\ (mg/L) = 50\ (\frac{(Al \times 3)}{27} + \frac{(Fe \times 3)}{56} + \frac{(Mn \times 2)}{55} + 1000 \times 10^{(-pH)})}$$

Figure 3.4 Acidity titration set up. pH temperature probe and magnetic stirrer both present in sample beaker, whilst ~0.5 mL increments of NaOH solution are added drop wise from burette.

3.6 Acidity Characterisation

Acidity characterisation through the use of titration curves has been covered in Section 2.6.1. Different acidic species will buffer out of solution across different pH ranges, which can be observed in the differing fluxes of a pH curve (Figure 2.6). However in addition, in terms of organic acid, there is the potential for a titration curve to identify weak (organic) acids (as seen in Figure 3.5). The initial upward curvature of the weak acid titration is distinctively different compared to a strong acid curve.

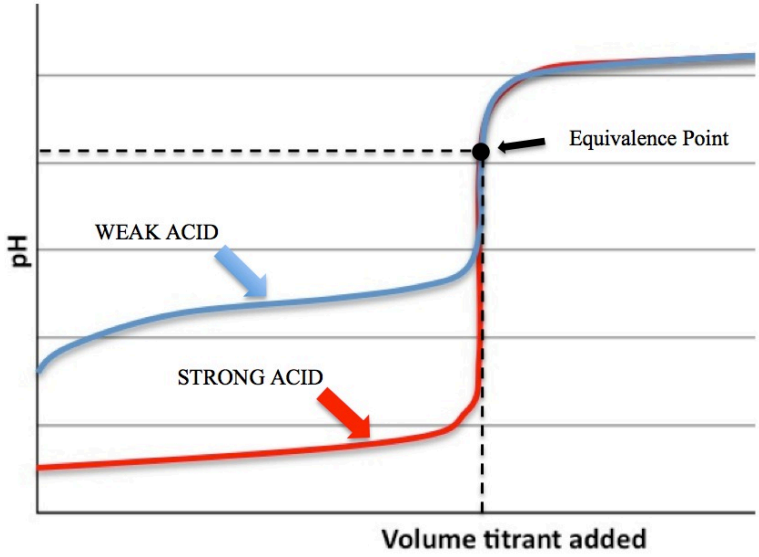


Figure 3.5 Difference between weak acid and strong acid titration curves

4 Analysis of archived RTIO and Environmental Monitoring Data

4.1 Introduction

This chapter presents a summary and analysis of the archived geochemical, biological and imaging data for Mt Tom Price Mine and explores how they may relate to the geochemical characteristics and acidity inconsistency issue in the SSIX pit. The raw data analysed in this chapter have been extracted from archived files (dating back to 2002) from the RTIO data management system (EnviroSys). The analyses and interpretations of data presented throughout this chapter are original to this thesis.

Annual aerial photos (2002-2011 and 2012 ground photos) record changes in the physical characteristics such as lake water height and colour in the SSIX pit.

A decade of annual climate data is presented, which has also been provided by RTIO (originally collected and archived from the local weather station operated by the Australian Bureau of Meteorology).

Surface water geochemical data from the on-site environmental monitoring programme's archive at Mt Tom Price is also presented in this chapter. These data provide important opportunities to explore the relationship between total and calculated acidity with respect to time, as well as annual changes in geochemical properties of the SSIX pit water.

Schoeller diagrams are used to compare the geochemical concentrations between specific SSIX pit water samples (see Section 3.3.3 for definition of Scholler diagrams), as well as between specific source water samples (surface and bore water), to determine any geochemical influence from source water on the SSIX pit

The chapter first presents the data collected from the initial 2007 investigation. These data constrain/help identify the geochemical and biological interactions contributing to and occurring within the SSIX pit and their relationship(s) to acidity inconsistencies.

The subsequent results and figures present the temporal variation in the geochemical analysis of bore and pit water samples, photographic images of the SSIX pit and climate data in the environment of the SSIX pit.

It should be acknowledged that, due to the sometimes low temporal resolution between recorded data (aerial photos) and the environmental monitoring programme (geochemical data), standard statistical analysis proved to be inappropriate to evaluate relationships between data sets in this project. Simple correlations between system interactions in the SSIX pit environment were assessed, such as rainfall versus ion concentrations as well as regression on moving average values for each correlation. Despite the trends that can be seen over time (in many of the graphs to follow), linear correlations proved to be statistically insignificant for the temporal datasets analysed. Further specific investigations conducted for this thesis in 2012 is presented in Chapter 5.

4.2 2007 investigation

This investigation was completed after the discovery of differing calculated versus total (titrated) acidity concentrations in the SSIX pit. In order to explain these differing acidities, the geochemical and biological properties of the pit water were determined in an effort to identify any potential irregularities contributing extra acidity. The 2007 investigation included geochemical data (determined by SGS laboratories) and biological analysis of phytoplankton densities, potentially producing organic acidity (determined by Dalcon Environmental laboratories), for water samples from the SSIX pit and some of the contributing surface and bore water sources.

Table 4.1 shows the geochemical analysis of the SSIX pit and some of its bore and surface water inputs (as of August, 2007). These data illustrate the key point of Section 2.4.1, and show that the concentrations of many elements in the SSIX pit water exceed the ANZECC stock water guidelines (Australia and New Zealand Environment Conservation Council) and the AWDG guidelines (Australian Drinking Water Guidelines) for SO_4, Al, Fe, Mn, Ni and Cu (Figure 4.2).

The Al, Fe, Mn, Ni and Cu concentrations, of the SSIX pit water geochemistry, when elevated may present phytotoxic conditions for algae. Further comparisons and discussion of the specific effects and trends created by excessive concentrations of these ions in SSIX are discussed in Section 4.6. The influence of source water input to the SSIX pit geochemistry is addressed further in Section 4.7.

Table 4.3 presents the phytoplankton count (as of August, 2007), which was completed on the same set of surface and bore water samples. The reported values (from Dalcon Environmental), demonstrate the considerable contribution of phytoplankton from bore and surface water inputs to the SSIX pit. The SSIX pit sample exhibits the highest phytoplankton count, with 392,040 cells m/L of chlorophyceae *Chlorophyte* 0.78 (characteristics and implications of this phytoplankton presence are described in Section 2.7.1 and Section 6.3, respectively). Dalcon Environmental also quantified a percentage of uncertainty in their identification of phytoplankton dataset. There is a chance for human error in identification of phytoplankton, which is clearly present in some of the original results (see Appendix IV).

Table 4.1 Reported geochemical analysis by SGS commercial labs, during the 2007 project scope investigation, for the related sites of surface water or bore water samples (31/08/2007). Highlighted: potentially phytotoxic major ions in solution and the SSIX pit column.

			Bore water contributors to SSIX				Surface water contributor to SSIX
Sample	Units	SSIX pit	WB05-SEP1	WB05-SEP2	WB03 -SEP01	SEP (DB3)	SEP Cyclone Tank
pH	pH units	3.58	5.52	5.19	5.04	4.17	-
Acidity as $CaCO_3$ (pH=8.3)	mg/L	280	210	250	230	270	220
Total Dissolved Solids @ 180°C	mg/L	560	220	270	500	760	460
Chemical Oxygen Demand	mg/L	9	<5	<5	<5	<5	<5
Aluminium, Al	mg/L	4.1	<0.02	0.05	0.53	5.1	1.9
Calcium, Ca	mg/L	22	9.7	7.0	23	26	17
Chloride, Cl	mg/L	99	82	84	130	81	91
Copper, Cu	mg/L	0.071	0.008	0.003	0.027	0.075	0.033
Iron, Fe	mg/L	1.6	0.22	5.2	<0.02	0.15	1.1
Potassium, K	mg/L	11	7.3	6.9	10	12	9.5
Magnesium, Mg	mg/L	53	16	25	38	76	44
Manganese, Mn	mg/L	2.2	0.005	0.40	0.82	3.5	1.5
Sodium, Na	mg/L	47	34	30	50	44	39
Nickel,Ni	mg/L	0.16	0.005	0.03	0.06	0.24	0.10
Zinc, Zn	mg/L	0.16	0.026	0.03	0.051	0.27	0.11
Silica, SiO2 #	mg/L	46	21	23	56	55	40
Sulphate, SO_4	mg/L	260	55	95	160	380	200
Nitrate, NO_3	mg/L	18	2.9	<0.2	40	16	15
Phosphorus, P	mg/L	<0.1	<0.05	<0.05	<0.05	<0.1	<0.05
Total Organic Carbon	mg/L	1.2	<1	<1	<1	<1	<1
Biological Oxygen Demand (filtered)	mg/L	<5	<5	<5	<5	<5	<5

Table 4.2 ADWG and ANZECC stock water guidelines. Showing the major ions and highlighted concentration guidelines of concern in the SSIX pit water

Analyte	ADWG Concentration (mg/L)		ANZECC Stock Water Guidelines (mg/L)
	Health	Aesthetic	
pH	-	6.5-8.5	6-8.5
TDS	-	500	5000
SO_4	500	250	1000 - 2000
Al	-	0.2	5
Cu	2	1	0.4
Fe	-	0.3	-
Mn	0.5	0.1	-
Ni	0.02	-	1

Table 4.3 The reported densities of the phytoplankton count, completed by Dalcon Environmental during the 2007 project scope investigation, for each related surface water or bore water sample (31/08/2007). Highlighted: phytoplankton count in the SSIX pit.

	Phytoplankton density count from each monitoring point $\left[\frac{cells\ m/L}{(\%)}\right]$					
Phytoplankton type	WB05 -SEP01	WB05 -SEP02	WB03 -SEP01	SEP Cyclone Tank	SSIX Pit	SEP (DB3)
Chlorophyceae *Chlamydonomas* sp.	88 (0.85)	44 (14.29)	-	-	-	-
Chlorophyceae *Chlamydonomas* sp. 010	88 (0.85)	-	-	-	-	-
Chlorophyceae *Chlorophyte* 078	-	-	-	-	392,040 (99.84)	264 (16.67)
Cyanobacteria *Synechocystis* sp. 002	1,188 (11.44)	44 (14.29)	-	44 (4.76)	616 (0.16)	-
Cyanobacteria *Synechocystis* sp. 003	9,020 (86.86)	220 (71.43)	3,652 (100)	880 (95.24)	-	1,320 (83.33)

4.3 Aerial photos

Aerial photos are collected by RTIO for the use of mine planning. Archived image files were obtained for the use of this project to identify changes in the SSIX pit over time.

The following images (Figure 4.1 and Figure 4.2) show a comparison of the same area of the SSIX pit across seasonal and annual periods. The frequency of when images are captured varies and thus ground shots had to be used for the comparison of 2012 images (Figure 4.3).

As mentioned in Section 1.3.3, the climate in the Pilbara changes dramatically between the wet season (December to March) and the dry season (August to November). One of the most salient features of the aerial photographs is the change in colour from the wet season to the dry season in the SSIX pit water. A brown colouration of SSIX pit water can be seen in photos taken during the wet season, followed later in the year by green coloured water during the dry season (with obvious notable exception of March 2008). Figure 4.2 further demonstrates that the colour changes occur independent of pit lake level (water volume), as the SSIX pit water level is artificially altered due to pumping from contributing bores and surface water sites.

During the 2007 investigation the green colour of the SSIX pit water was hypothesised to be algal growth and consequently proved by the phytoplankton count (Table 4.3). This record of phytoplankton as the cause of green water, was originally utilised in this thesis. However from observation of aerial photo collection it can be verified that there seems to be two types of green colourations, opaque green and translucent green (categories OG and TG; Figure 4.1 and Figure 4.2). The colour categories given for each photo have thus been labelled to distinguish between the two greens and the brown water colour (category B; Figure 4.1 and Figure 4.2), which can also be seen in the ground photos of 2012. This variation of water colour will be referred to in further discussion (of Chapters 4, 5 and 6) once geochemical, biological and imagery comparisons have been made with the data collected in 2012 as part of this thesis.

It should be noted that there is the potential for errors when assigning colour categories based on archived photos (e.g. due to interference with brightness or sun shadows). Pit water colour will also be sensitive to weather conditions (e.g. the obvious shadow in Figure 4.1; 06-2004) during the period immediately before and during each individual photographic capture.

Archived aerial photos from other relevant locations in the Mt Tom Price mine area were also screened (such as the SEP pit). These additional aerial photos are not presented here due to a lack of significant identifiable features and changes through time.

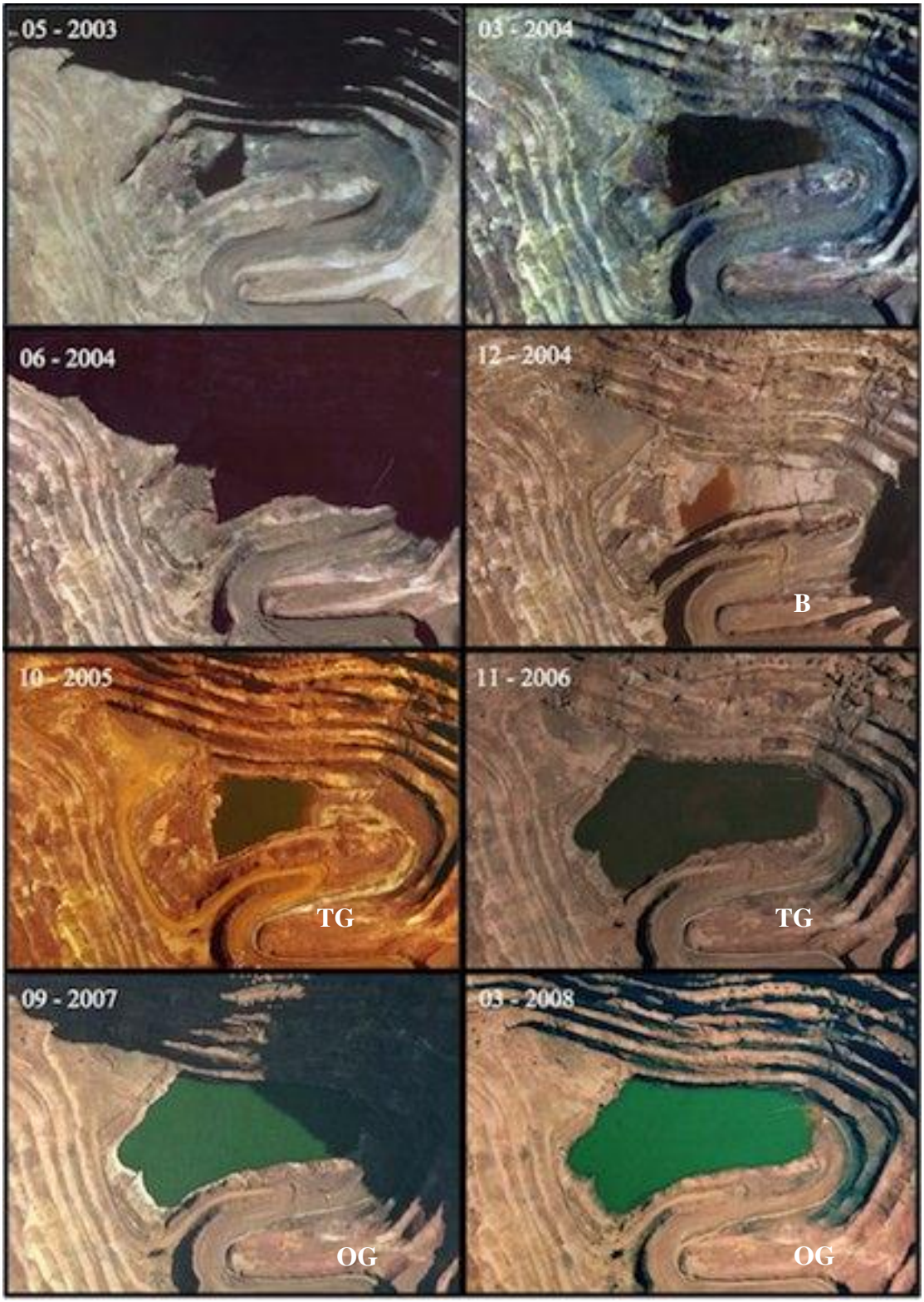


Figure 4.1 RTIO archived and dated aerial photographs of the SSIX pit (2003 – 2008). Water colour categories: OG = Opaque green. TG = Translucent green. B = Brown.

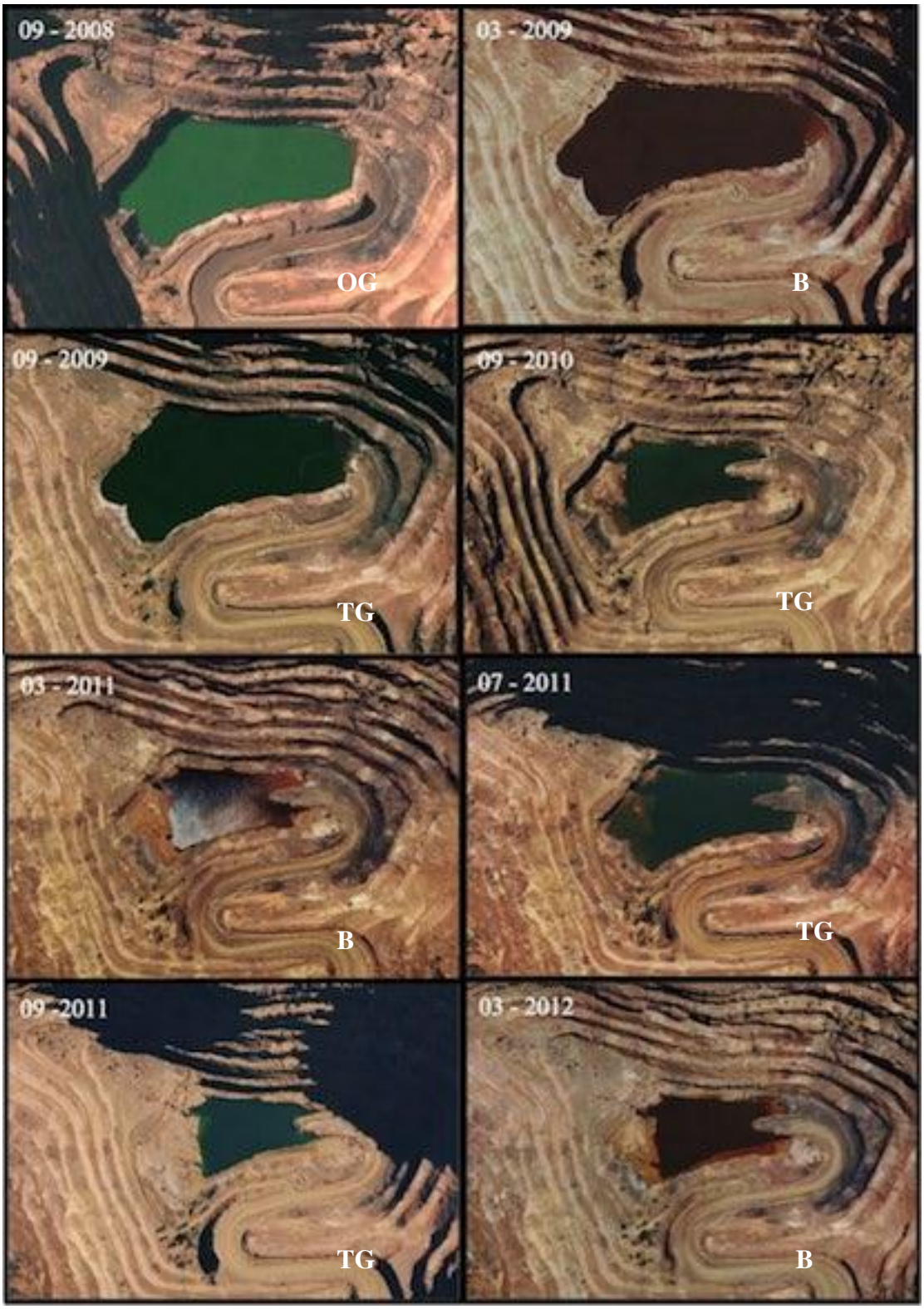


Figure 4.2 RTIO archived and dated aerial photographs of the SSIX pit (2008 -2012) Water colour categories: OG = Opaque green. TG = Translucent green. B = Brown.

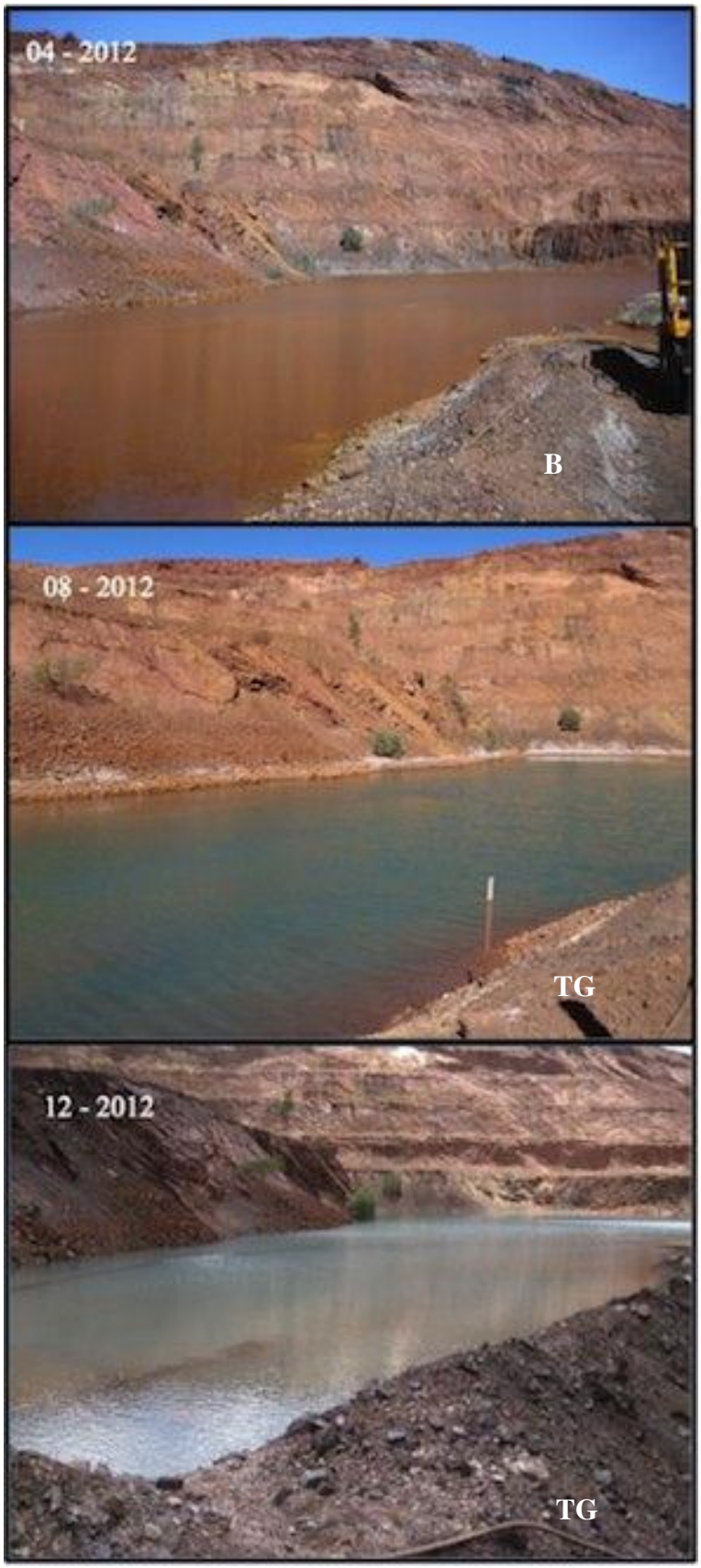


Figure 4.3 Dated ground photographs of the SSIX pit during 2012 investigation. Water colour categories: B = Brown. TG = Translucent green.

4.4 Climate data

Due to the potential linkages between seasonal climate changes and SSIX pit water conditions, it is important to present meteorological data relevant to the time period studied. The climate graph presented in Figure 4.4 shows the rainfall and temperature record at Mt Tom Price over a decade of observations made by RTIO. From this graph the RTIO weather data show a clear seasonal pattern, with a few larger rainfall events scattered across wet seasons. The wet annual periods that experience above average total rainfall (>366.7 mm) have been highlighted in Table 4.4 below. Peaks in annual rainfall occur in summer when the temperatures are at their highest. It was expected that any irregular climate sequence would be reflected by a change in SSIX pit environment and water geochemistry and biology. Once again, pit water volume in the SSIX pit does not appear to be directly dependent to rainfall (as seen in the aerial photos), due to pumping schedules. However, rainfall influences on pit water geochemistry and major ion concentrations will be presented in the following sections.

Figure 4.5 shows how regular climate variations are also reflected in the water temperature of the SSIX pit. This is useful information to consider when analysing the system interactions (geochemical and biological), because it is thus known that the pumping of water into SSIX does not interfere with the water temperature, which is dictated by the climate.

Further discussion of the climatic effects discussed here will continue throughout Chapters 4, 5 and 6.

Table 4.4 Total annual rainfall compared to average annual rainfall. Above average annual periods are highlighted (yellow).

Year	Total Rainfall (mm)
2002	284.3
2003	225.2
2004	430.5
2005	286.2
2006	711
2007	218.8
2008	558.4
2009	524.8
2010	114.2
2011	294.2
2012	386.2
Annual Average	**366.7**

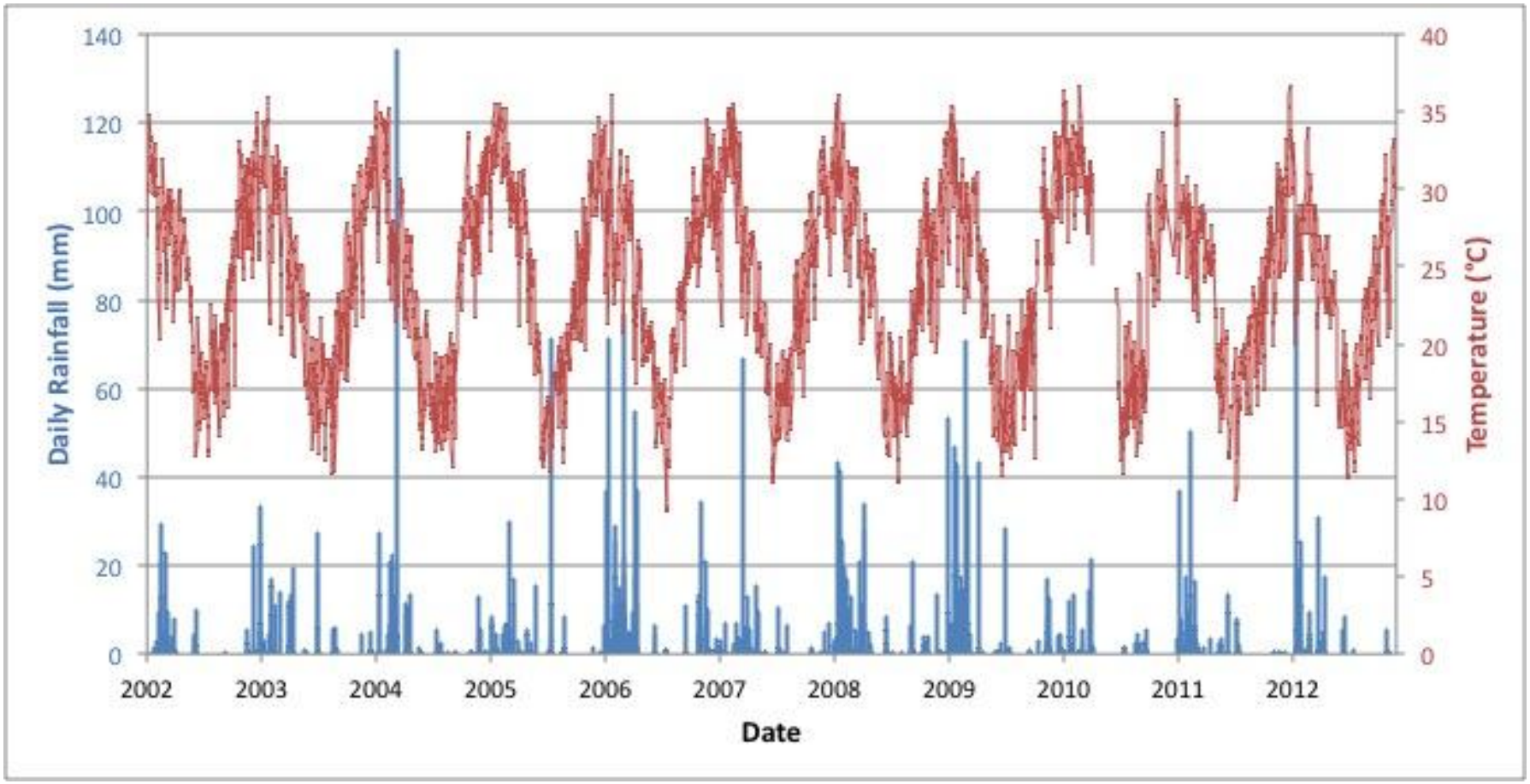


Figure 4.4 Climatograph of Mt Tom Price mine daily rainfall and temperature (for the past decade).

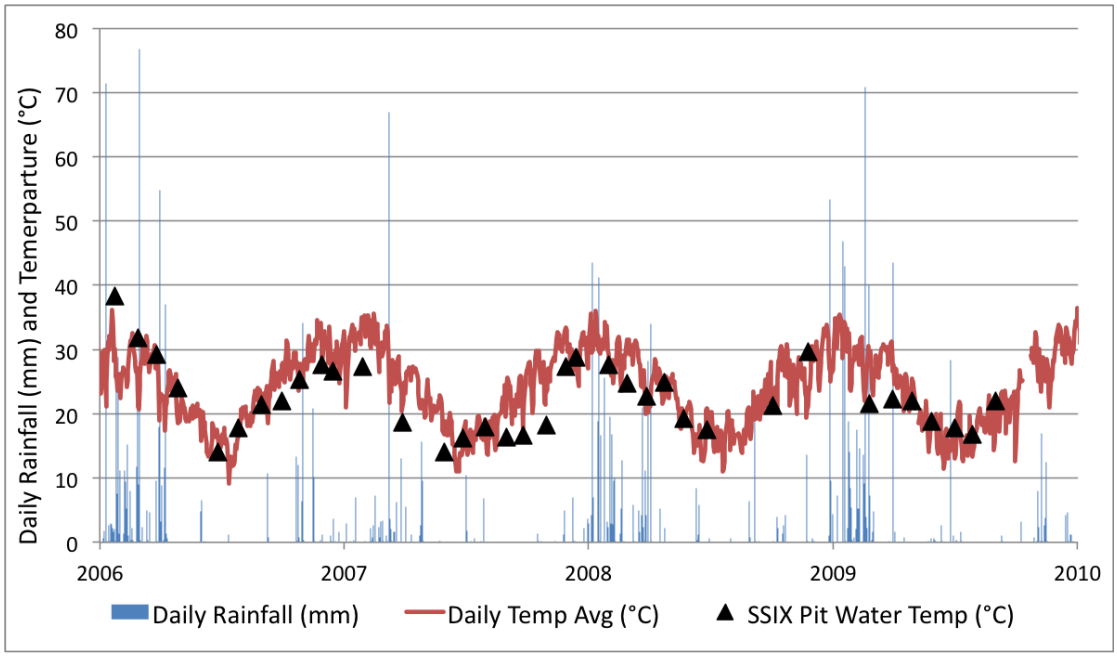


Figure 4.5 Climatograph of Mt Tom Price mine climate, including example of the water temperature trend of the SSIX pit.

4.5 Total and calculated acidity

The comparison of total and calculated acidities, from a water body over time, have the potential to explain a large amount of the variance in water geochemistry. In the case of the SSIX pit, this is exactly what was identified in 2007, with the calculated acidity of 45 mg/L (as $CaCO_3$) and a total acidity (completed by hot acidity titration) of 280 mg/L (as $CaCO_3$; Brown, 2007).

Figure 4.6 presents nearly a decade of acidity data from the SSIX pit. The differences between total acidity and calculated acidity can be seen by the concentration difference between each plotted point above the timeline. RTIO used to perform cold acidity titrations for determining total acidity, but have since changed to hot titrations due to the diminished buffering effects caused by pre-treatment and removal of hydrolysable metal ions, resulting in a more accurate acidity value (see Section 2.6.2 for explanation of cold and hot titrations methods). The exact date when this titration method changed is unknown, but it is known to be prior to 2007.

As can be observed from 2006 to 2007 on this timeline, there seems to be quite a large difference between the calculated and total acidity. This either suggests cold titration buffering effects or the presence of a non-calculable acidic substance in the water

geochemistry. In terms of the 2007 investigation, these inconsistent acidity values where hypothesised to be due to an organic acid caused by the algal presence. The role of algae had initially been suggested due to the green colouration of the pit lake water. This was concluded by the phytoplankton count completed by Dalcon Environmental (Table 4.3). However, any presence of organic acidity by titration or acidity speciation was not reported by RTIO.

Conversely, in the region from 2008 to 2010 there is a much closer relationship between the calculated and total acidity. This could be explained by visual inspection of the acidity and rainfall intensity time-series records (Figure 4.7), which suggests that there is a (weak) relationship between these two parameters. When a large rainfall event occurs there is a closer comparison between the calculated and total acidities (e.g. circled area in 2008-2010, Figure 4.7). Such relationships could be related to a peak in metal concentrations, i.e. those that make up the calculated acidity (Al, Fe and Mn). This idea will be explored further in Sections 6.4.2.

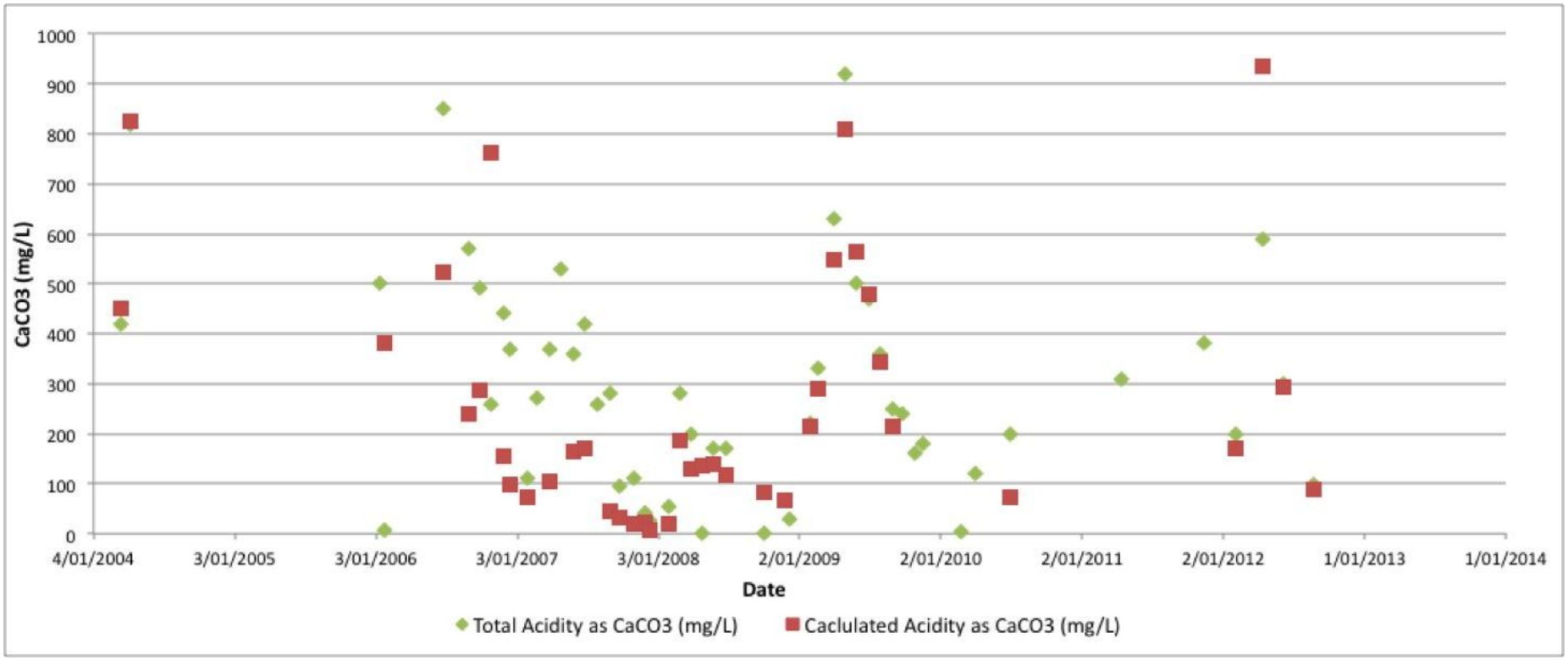


Figure 4.6 Comparison of the total acidities and calculated acidities derived from the SSIX pit water geochemistry over time.

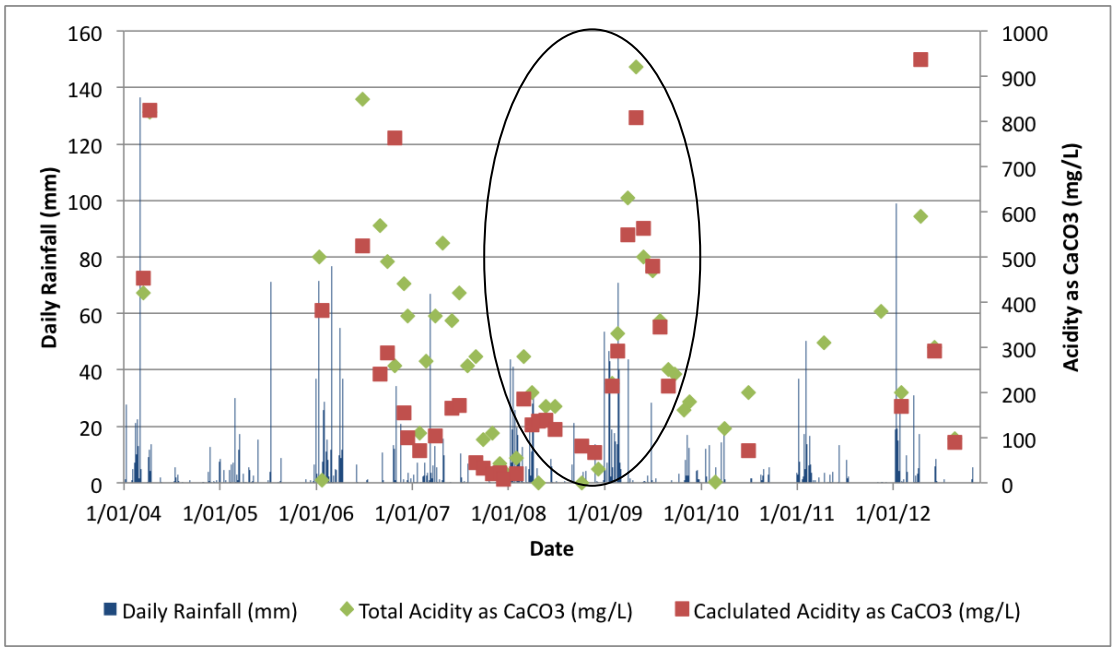
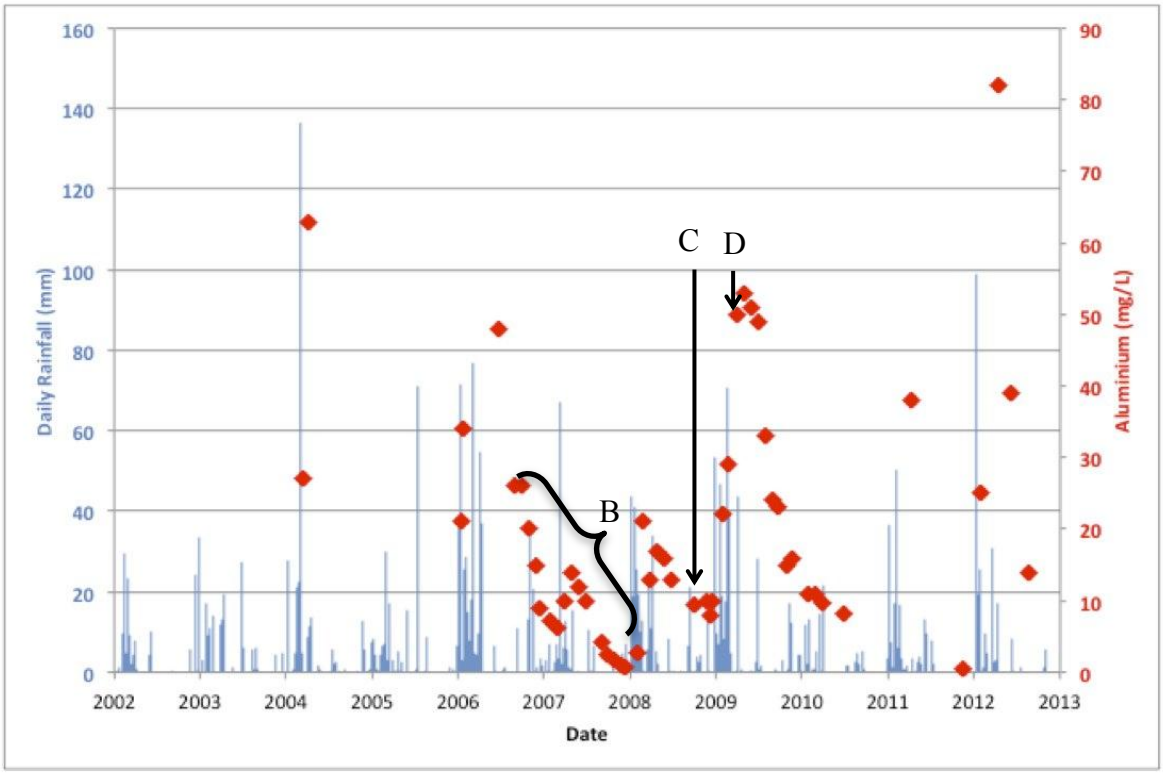


Figure 4.7 Comparison of the SSIX pit water total acidity and calculated acidity concentrations over time and in relation to rainfall. The 2008 and 2009 period (circled) shows that after a dense period of rain, where a peak in both acidities occurs, minimal difference is observed between acidity concentrations.

4.6 Metal ions

A substantial amount of water geochemistry data has been collected, for the past decade, during the Environmental Monitoring programme at Mt Tom Price mine. Time-series plots of major ion concentrations and physical characteristics of the SSIX pit (pH and rainfall) are presented in the following multi-figures. Each multi-figure exhibits a trend with seasonal rainfall fluctuations (or major rainfall events) and an increase in ion concentrations. This pattern was not expected; high rainfall should dilute ion concentrations. However, major rainfall events are increasing ion concentrations perhaps due to increased hydrolysation of exposed minerals (highly soluble minerals such as sulphates) from rainfall runoff on the pit walls (which may also recharge groundwater aquifers).

The first multi-figure (Figure 4.8) shows the changes in aluminium concentrations during fluctuations in rainfall and pH, in the SSIX pit. Comparisons are also made with the concentrations of other major ions and pit water colour, during specific samples/periods (to help determine any potential influential factors in aluminium concentration). Figure 4.8

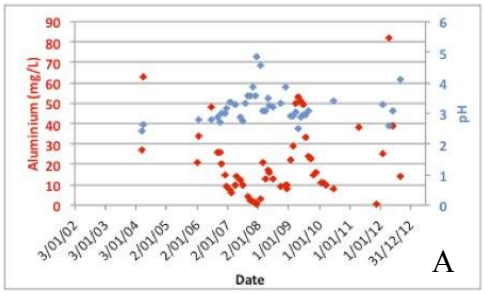


A = Aluminium (mg/L) compared to pH of SSIX pit water.

B = Constant decline of all ions, including aluminium, in 2007.

C = Opaque green colouration of SSIX pit during low concentration of aluminium.

D = Brown colouration of SSIX pit during high concentration of aluminium.



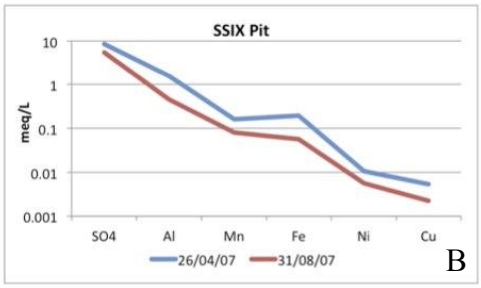


Figure 4.8 Multi-figure showing the connections between Al concentrations in the SSIX pit alongside rainfall, pH behaviour, similar ion concentrations and aerial photography showing pit lake colouration.

presents aluminium concentration and rainfall with respect to time. As was seen for other dissolved phases, aluminium concentrations appear to covary with rainfall amount. For example, an intense period of rainfall in 2006 is contemporaneous with a peak in aluminium concentration followed by a gradual decline until the next intense rainfall event in 2008. The same pattern recurs in 2009. The relationship between aluminium concentration and pH (Figure 4.8A) shows the expected trend of increasing concentration with decreasing pH, due to the elevated solubility of aluminium ions in acidic conditions. Similar concentration changes of the other major ions in the SSIX pit (following the 2006 intense rainfall event between the 2007 wet and dry season), can be identified by the Scholler diagram (Figure 4.8B). The concentrations of aluminium are strongly related to pit water colour categories. When there is a low concentration of aluminium the pit water appears opaque green (Figure 4.8C; potential algae bloom) and when there is a high (potentially toxic) concentration of aluminium, the pit water appears brown (Figure 4.8D; suggesting no algal presence).

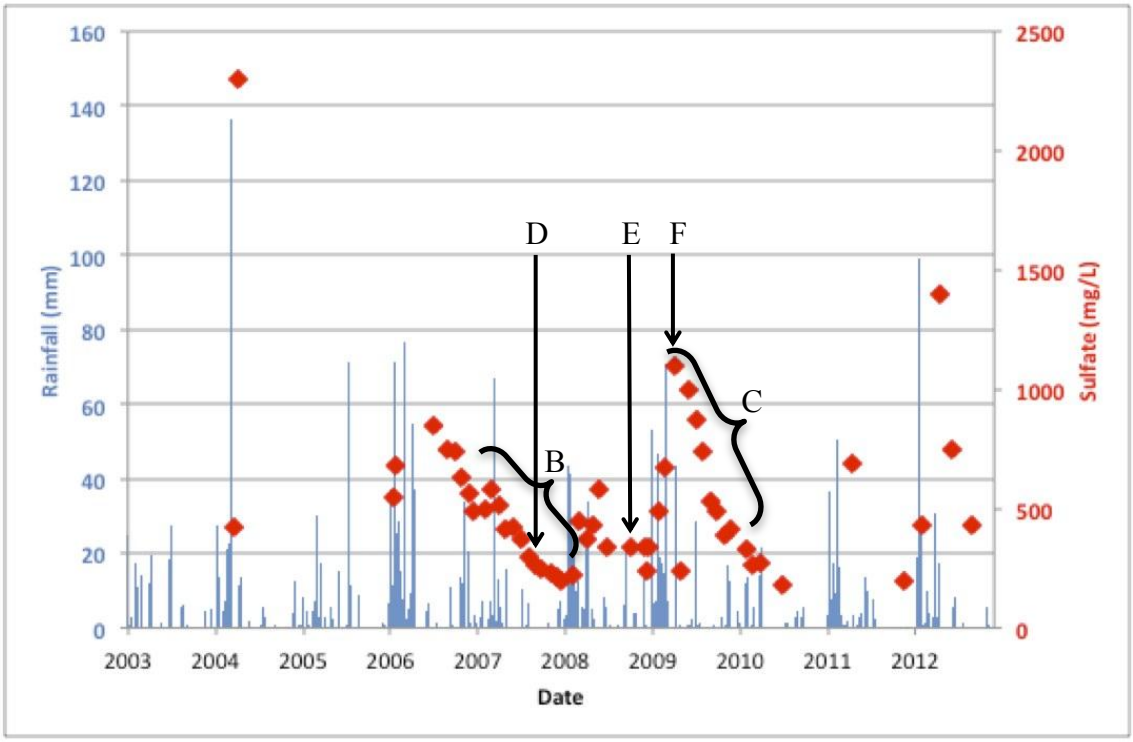
When relating increased rainfall trends to the volume of pumped water into the SSIX pit, it can be seen that the volume of water does not always influence water geochemistry. The 2007 Tom Price Annual Environmental Report (RTIO, 2007) includes monthly flow data for discharge pumped into the SSIX pit (Table 4.5). Similar volumes, of pumped discharge to the SSIX pit, are presented for April and August 2007 despite the differing major ion concentrations shown in the 2007 Schoeller diagram (Figure 4.8B). Thus concluding the minimal effect water volume has on pit water geochemistry. It is more likely the pumped water contributes its own geochemical characteristics to the SSIX pit, independent of the geochemical input from rainfall runoff. These ideas will be further discussed in Section 4.7 and Section 6.2.1 respectively.

The pump data (Table 4.5) also shows a larger total discharge volume in 2007 than in 2005, despite the lower (below average) total rainfall in 2007 (Table 4.4). This could potentially be due to continued pumping from the effects of the large rainfall accumulation of 2006.

Table 4.5 Total monthly flow values for discharge input to the SSIX pit, for 2005 - 2007. Highlighted: the relatively similar pump flow volumes into SSIX for April and August 2007, despite changes in water geochemistry; see Figure 4.8 B. (RTIO, 2007)

Month	Total Monthly Flow (m^3) 2005	Total Monthly Flow (m^3) 2006	Total Monthly Flow (m^3) 2007
January	-	70,011	16823
February	-	72,680	29877
March	-	49,906	26813
April	17,300	39,381	29332
May	20,829	54,228	36463
June	22,412	70,703	29499
July	12,439	30,355	22120
August	22,698	41,584	30307
September	19,765	21,868	20513
October	1,392	32,637	33387
November	13,738	37,023	34630
December	53,108	51,866	22843
TOTAL	**183,681**	**572,242**	**332,607**

Similar trends can be identified in the multi-figure of Figure 4.9, presenting sulphate concentrations in the SSIX pit. A strong decline can be seen with sulphate concentrations across the 2006-2008 period as well and the 2009 period. This sulphate concentration decrease can, once again, be related to decreased rainfall events. It is more apparent in this figure (than in Figure 4.8) that rainfall is extremely concentrated during the wet seasons of 2006, 2008 and 2009. These bursts of meteoric water appear to correlate with elevated sulphate concentrations (i.e. soluble sulphates). It would be assumed, from this graph, that a strong correlation could be made due to these obvious features. However linear regression analysis was undertaken and proved non-significant, with a correlation coefficient of -0.118. The trends formed will still be used for discussion.

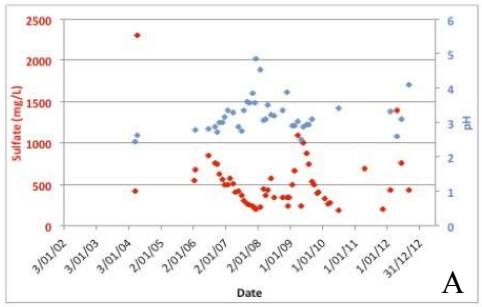


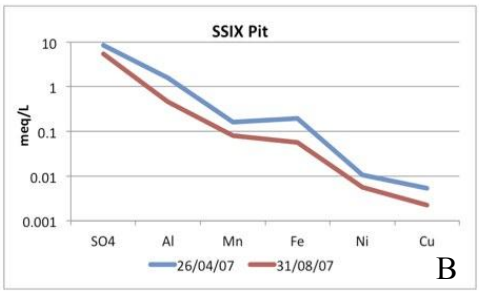
A = Sulphate (mg/L) compared to pH of SSIX pit water.

B & C = Constant decline of all ions, including sulphate, in 2007 & 2009.

D & E = Opaque green colouration of SSIX pit during low concentrations of sulphate.

F = Brown colouration of SSIX pit during high concentration of sulphate.





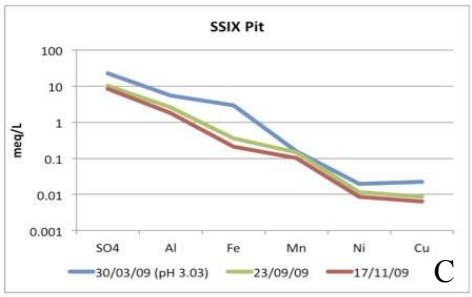
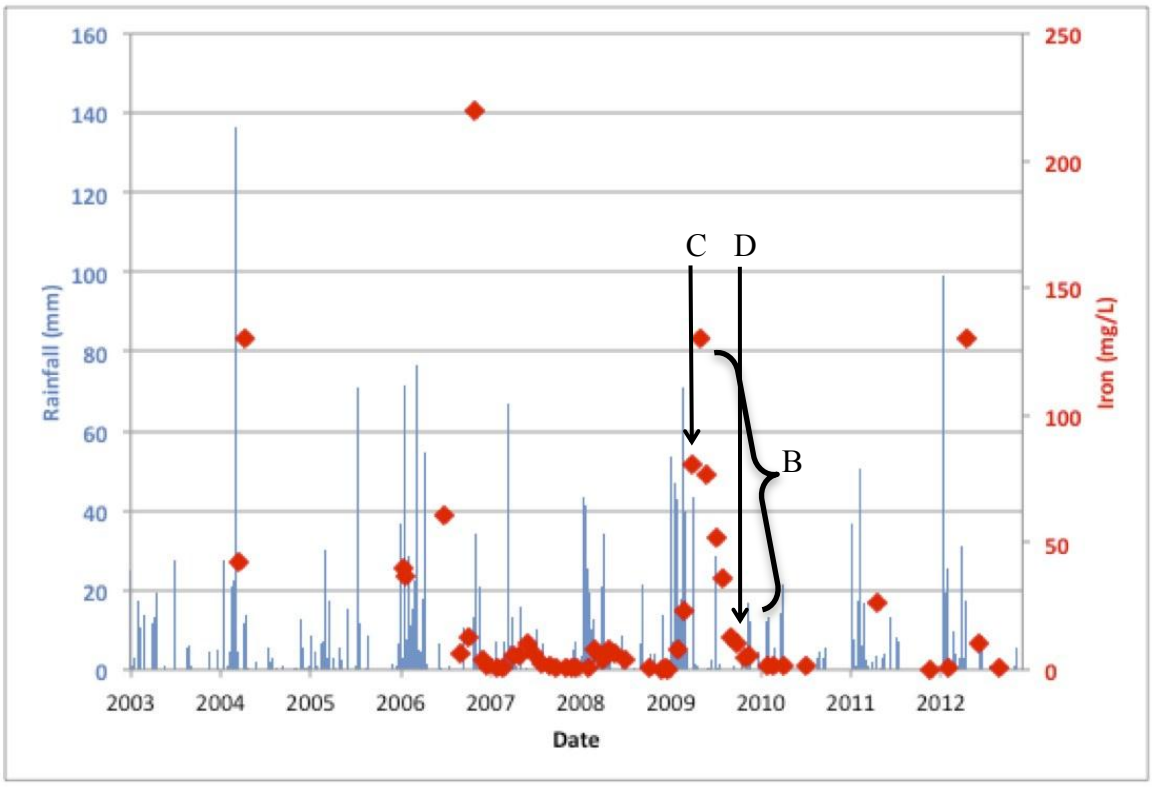


Figure 4.9 Multi-figure showing the connections between SO_4 concentrations in the SSIX pit alongside rainfall, pH behaviour, similar ion concentrations and aerial photography showing pit lake colouration.

Figure 4.10 shows the multi-figure trends for iron concentrations in the SSIX pit. This figure shows the same relationships with rainfall and pit water colour as seen for both Al and SO_4. However, there does appear to be lower magnitude elevations relative to baseline concentrations, except for the 2009 period. This less pronounced/extreme excursions can also be seen in the relationship between iron concentration and pH; Figure 4.10A shows little pH change during the major peaks in iron. Upon closer inspection, it was recognised that there are missing data points after the 2006 intense rainfall period; although speculative, perhaps there would be a peak in iron concentrations following the 2006 wet season, had they been collected at that time. There is also the potential that source water geochemistry, input to the SSIX pit, influenced/promoted the elevated periods of iron concentrations.

Figure 4.11 presents the concentration time-series for manganese. With similar fluctuations in manganese concentrations concurrent with rainfall periods (as seen with iron, aluminium and sulphate). However, the aerial photos reveal a different story for manganese. Relatively high concentrations of manganese occur during a period of translucent green colour in the pit water (both in late 2005 and 2006). This suggests that either manganese is a non-toxic metal for algae growth, or that the transluscent green colour reflects a different water geochemistry (perhaps coloured sulphates?) compared to the opaque green colour - more likely associated with episodes of extreme algal growth (e.g. 2007, 2008). Of course, both of these possible conditions may be true as well.

With respect to copper (Figure 4.12), elevated concentrations can be seen during translucent green periods in late 2005 and late 2006 and again in late 2009 (as shown in Figure 4.12E), as was observed with manganese. However, there is an extremely low concentration of copper when the opaque green water colour occurs (Figure 4.12D). Relatively low concentrations of nickel also occur during this opaque green water state (late 2008; Figure 4.13D). Furthermore, nickel concentrations show the common covariation with rainfall and is associated with brown water colouration (Figure 4.13E) during periods of elevated concentration. In order to fully understand the differences in pit water colour, geochemistry and algal growth further specific investigation into the SSIX pit have been undertaken in 2012. Chapter 5 presents results collected for this thesis, chosen to display the relationship between algal presence and acidic species (geochemical or organic) in the SSIX pit.

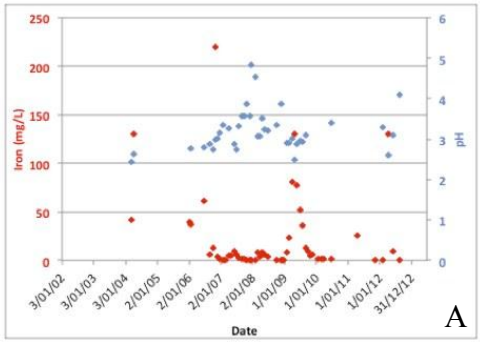


A = Iron (mg/L) compared to pH of SSIX pit water.

B = Constant decline of all ions, including iron, in 2009.

C = Brown colouration of SSIX pit during high concentration of iron.

D = Translucent green colouration of SSIX pit during low concentration of iron.



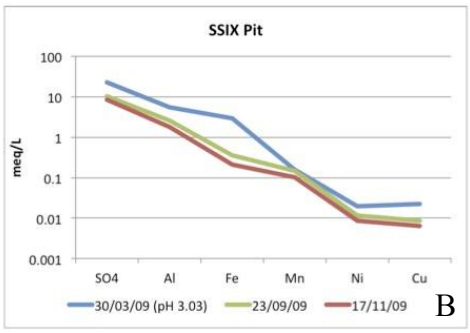
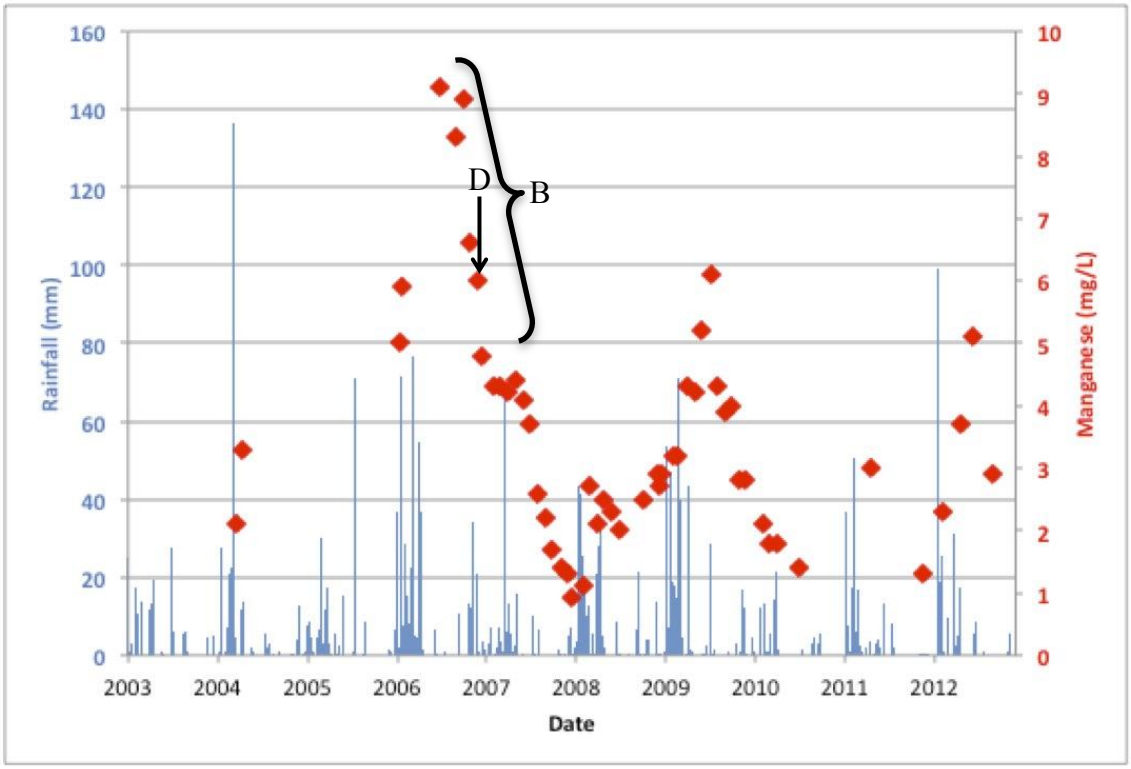


Figure 4.10 Multi-figure showing the connections between Fe concentrations in the SSIX pit alongside rainfall, pH behaviour, similar ion concentrations and aerial photography showing pit lake colouration.

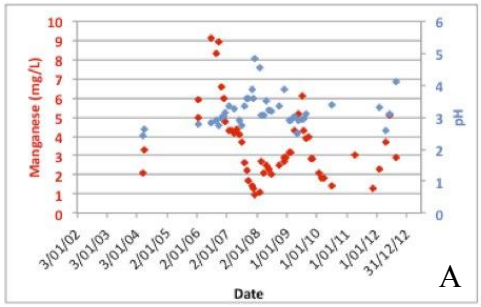


A = Manganese (mg/L) compared to pH of SSIX pit water.

B = Constant decline of all ions, including manganese, in 2006.

C = Translucent green colouration of SSIX pit.

D = Translucent green colouration of SSIX pit during high concentration of Mn.



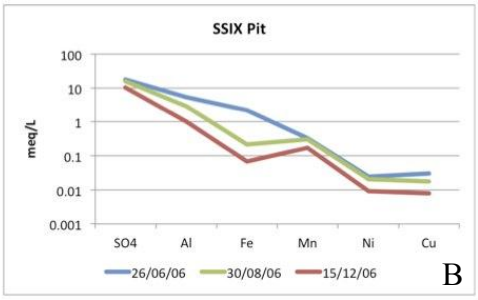
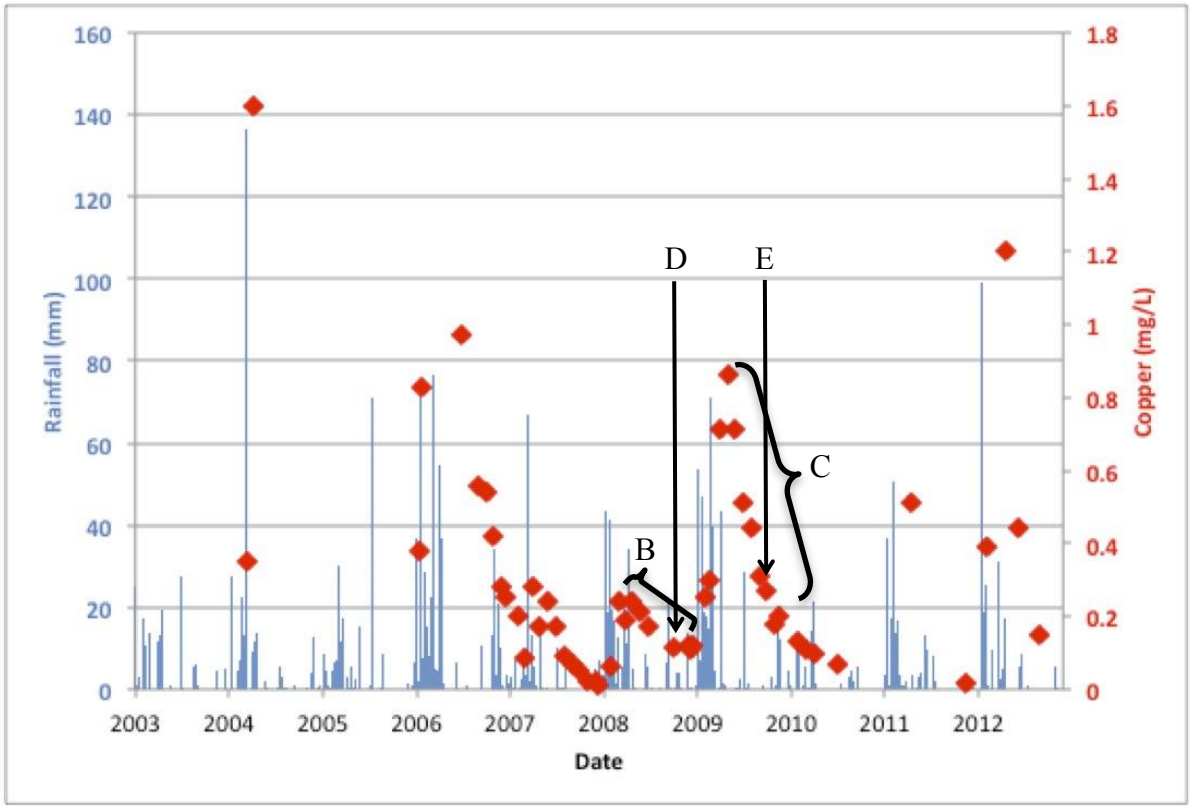


Figure 4.11 Multi-figure showing the connections between Mn concentrations in the SSIX pit alongside rainfall, pH behaviour, similar ion concentrations and aerial photography showing pit lake colouration.

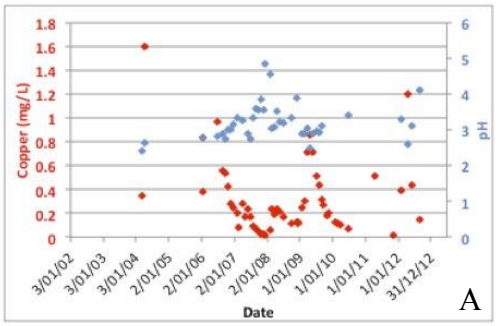


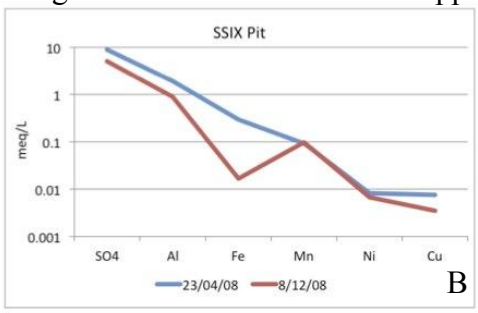
A = Copper (mg/L) compared to pH of SSIX pit water.

B & C = Constant decline of all ions, including copper, in 2008 & 2009.

D = Opaque green colouration of SSIX pit during low concentration of copper.

E = Translucent green colouration of SSIX pit during medium concentration of copper.





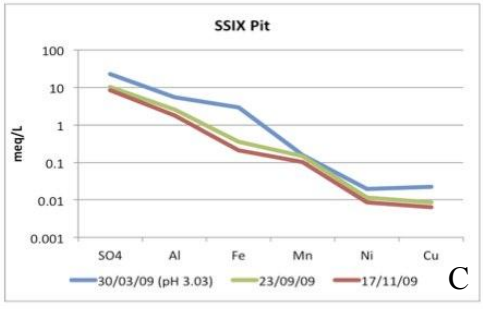
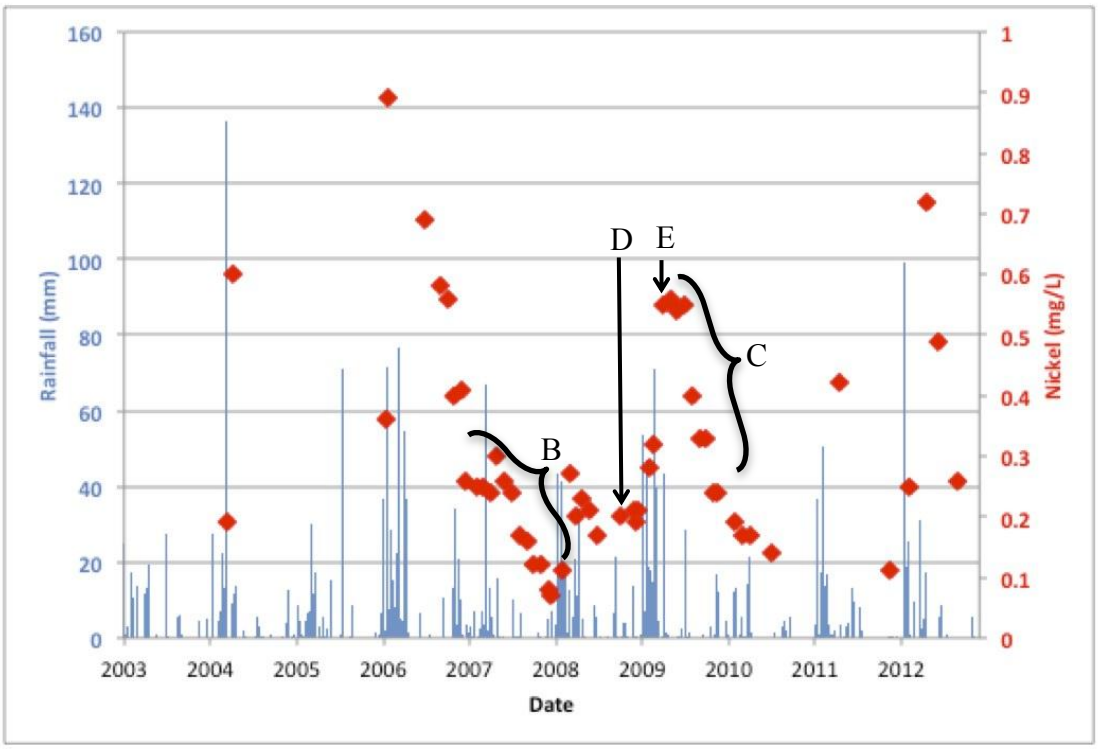


Figure 4.12 Multi-figure showing the connections between Cu concentrations in the SSIX pit alongside rainfall, pH behaviour, similar ion concentrations and aerial photography showing pit lake colouration.

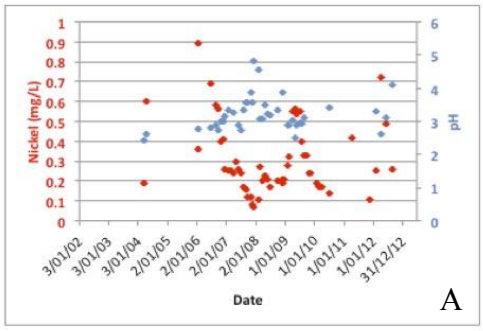


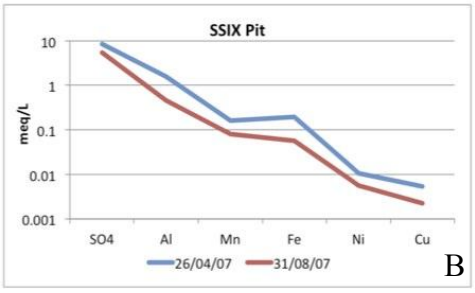
A = Nickel (mg/L) compared to pH of SSIX pit water.

B & C = Constant decline of all ions, including nickel, in 2007 & 2009.

D = Opaque green colouration of SSIX pit during low concentration of nickel.

E = Brown colouration of SSIX pit during high concentration of nickel.





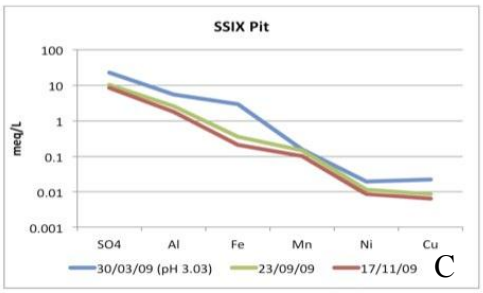


Figure 4.13 Multi-figure showing the connections between Ni concentrations in the SSIX pit alongside rainfall, pH behaviour, similar ion concentrations and aerial photography showing pit lake colouration.

4.7 Contributing bore and surface water data

The covariation between major ion concentrations and intense periods of (seasonal) rainfall shown in the previous section, can be further explored through comparison of the wet versus dry season concentrations of each major ion using Schoeller diagrams.

The Schoeller diagrams presented in this section clarify the relationship between ion concentrations during wet and dry seasons in the SSIX pit for 2009, 2010 and 2011. The value of these diagrams is the potential to add contributing bore and surface water data (source water to the SSIX pit) using a common graphical format. It is important to compare the source waters of the SSIX pit, to thus determine whether there is a large influential effect from the water inputs rather than the assumed rain-derived sources, on major ion concentrations presented in this chapter. Any major input from the source waters to the SSIX pit may justify the potential that source water also inputs algae or organic acid to the SSIX pit.

The contributing bore water samples to the SSIX pit water are likely to have some influence on the SSIX pit water geochemistry. This is best demonstrated by the bore water samples that exhibit a similar pattern between wet and dry seasons in the Schoeller diagram as the SSIX pit (Figure 4.14 - Figure 4.16). However, it is equally interesting to note that some bore samples do not exhibit this seasonal pattern, most likely due lower hydrologic permeabilities. These non-seasonal bore water inputs thus have the potential to dampen the seasonal changes in SSIX pit water geochemistry.

There is also potential for delayed leaching of major ions, from surface rainfall runoff, to groundwater (bore water samples). This should be noted as another variable when analysing these Schoeller diagrams (Figure 4.14 - Figure 4.16), which have the potential to indicate delayed geochemical input from bore water samples to the SSIX pit, compared to rainfall runoff inputs that have already occurred in the SSIX pit.

Figure 4.14 includes Schoeller diagrams for the major ion concentrations in the wet and dry seasons of 2009 (along with the available pH data). The SSIX pit concentrations show a consistent decline throughout the year. This pattern however, is only mimicked by the WB06SEP01 bore. All other bores (WB05SSIX1, PZ05SSIX2A, PZ05SSIX2B) exhibit elevated major ion concentrations during the dryer seasons.

In contrast the 2010 Schoeller diagrams (Figure 4.15) show a completely different trend, with very little difference between wet and dry seasons. This could most likely be due to the low rainfall in the wet season of 2010 (i.e. 21% of the 2009 rainfall), which lowers the influence of leached major ions into the bore water samples from surface rainfall runoff.

The 2011 Schoeller diagrams (Figure 4.16) show elevated concentrations are now present in most major ions during the wet season. This is perhaps a result of a higher rate of leaching due to the increased rainfall in 2011 (over double the 2010 rainfall; Table 4.4).

Unfortunately this thesis is unable to display pump data for 2009 – 2011, but increased periods of bore water pumping (discharge to SSIX pit) could potentially effect groundwater flow rates/leaching times and influence the geochemical status of a bore water sample.

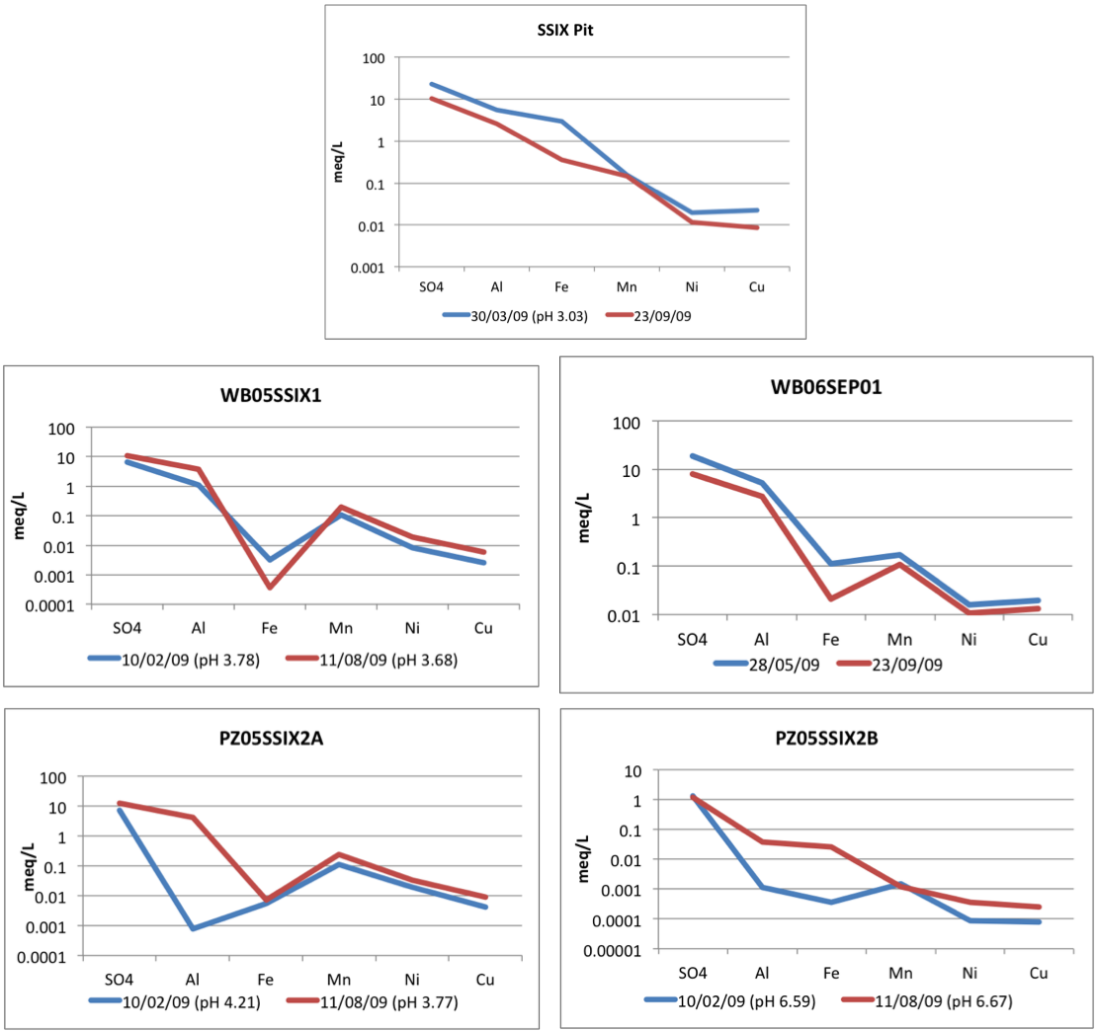


Figure 4.14 Comparison of ion concentrations across the 2009 wet (blue) and dry (red) seasons in the SSIX pit water samples related to geochemical data from contributing bore water samples.

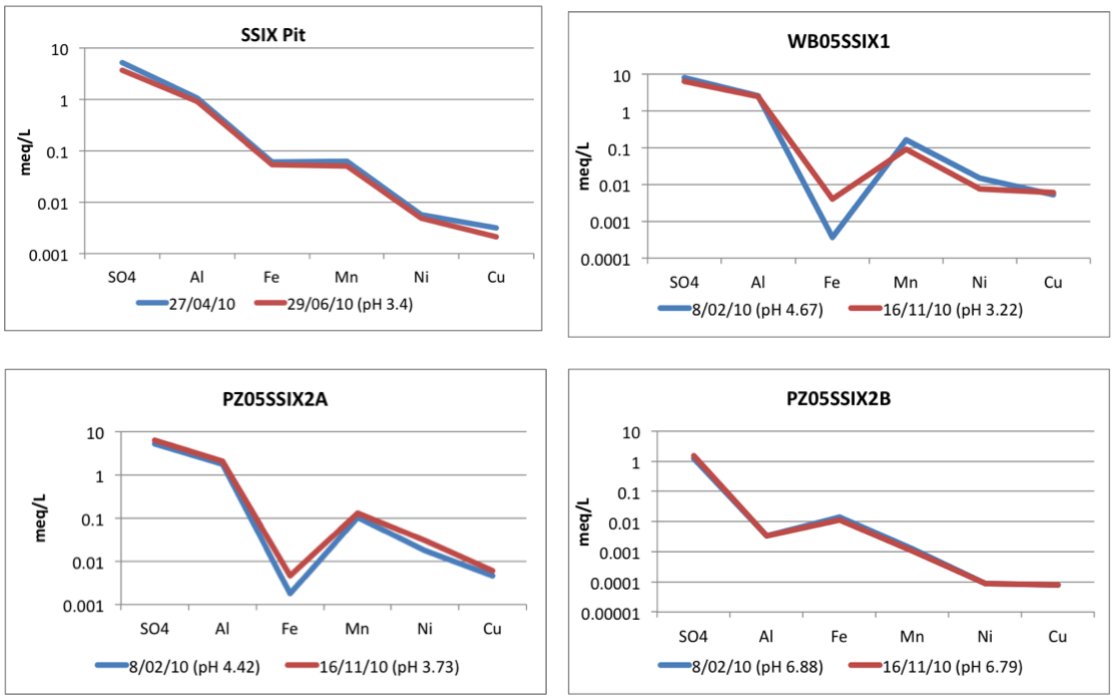


Figure 4.15 Comparison of ion concentrations across the 2010 wet (blue) and dry (red) seasons in the SSIX pit water samples related to geochemical data from contributing bore water samples.

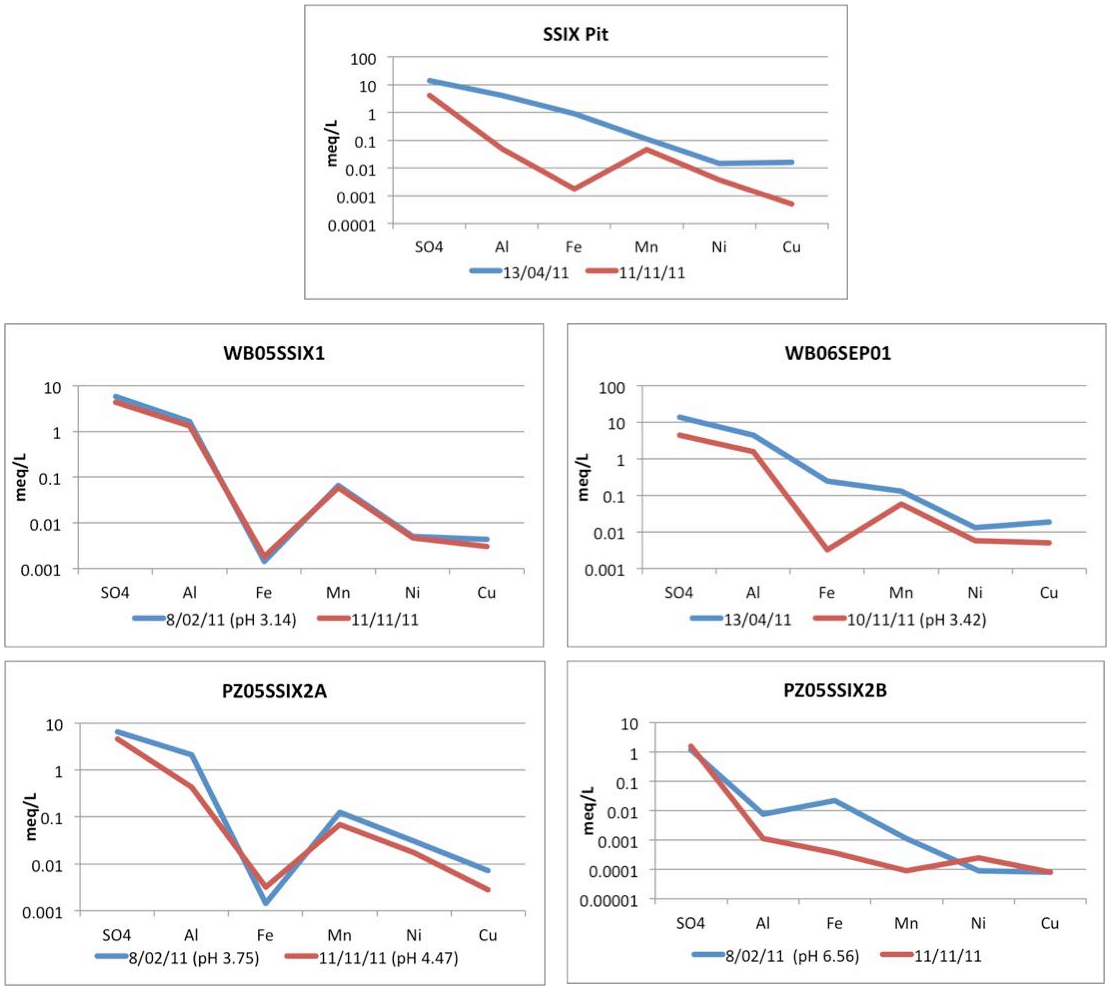


Figure 4.16 Comparison of ion concentrations across the 2011 wet (blue) and dry (red) seasons in the SSIX pit water samples related to geochemical data from contributing bore water samples.

Table 4.6 displays the geochemical data for total discharge input to the SSIX pit for the years 2005-2007 (RTIO, 2007). This discharge is a combination of all contributing water sources from the SEP to the SSIX pit. Table 4.6 shows the lowest concentrations of geochemical constituents in 2007, unsurprisingly when the algal growth was present. However when compared to Table 4.5 and the high total volume discharge input to the SSIX pit in 2007, it can once again be determined that water volume is generally unrelated to water body's geochemical composition. Table 4.6 further concludes that there is a major influence on geochemical constituents from source waters. This will be highlighted again in Section 6.3.

Table 4.6 Geochemical constituents of the discharge to SSIX, during 2005 – 2007. (RTIO, 2007). Highlighted: Low concentrations of input to the SSIX pit, during a period of confirmed algal presence.

Parameter	Units	2005	2006	2007
Acidity	mg/L	97.8	569.2	155.5
Aluminium	mg/L	5.6	37.7	3.4
Arsenic	mg/L	0.002	0.309	0.0005
Cadmium	mg/L	0.000	1.174	0.0001
Calcium	mg/L	21.2	32.4	20.1
Carbonate	mg/L	<1	<1	<1
Chemical Oxygen Demand	mg/L	7.5	46.1	<5
Chloride	mg/L	90.3	73.3	88.7
Chromium	mg/L	0.004	3.982	7.00
Cobalt	mg/L	0.107	0.356	0.087
Copper	mg/L	0.211	0.677	0.087
Electrical Conductivity	uS/cm	1140	1247	855
Iron	mg/L	11.2	47.6	3.148
Lead	mg/L	0.002	0.011	0.0105
Magnesium	mg/L	54.8	70.2	47.4
Manganese	mg/L	3.7	9.3	1.8
Mercury	mg/L	0.0002	0.0188	0.00036
Molybdenum	mg/L	<0.01	<0.01	<0.01
Nickel	mg/L	0.22	2.54	0.12
Nitrate	mg/L	24.20	48.70	18.78
pH		3.82	3.39	4.55
Potassium	mg/L	11.58	15.74	10.87
Selenium	mg/L	<0.005	0.05	<0.005
Silicon Dioxide	mg/L	55.5	72.5	38.75
Sodium	Mg/L	42.3	40.2	45.8
Sulphate	mg/L	332.5	668.0	252.5
Temperature	°C	30.0	25.7	25.2
Total Alkalinity	mg/L	<5	<5	NR
Total Dissolved Solids	mg/L	645	1064	532.5
Total Recovered Hydrocarbons (TRH)	mg/L	5.5	<0.5	<0.5
Total Suspended Solids	mg/L	<0.2	382	6.2
TRH C10-C14	mg/L	<0.04	<0.04	<0.04
TRH C15-C28	mg/L	<0.04	<0.2	<0.2
TRH C29-C36	mg/L	<0.2	<0.2	<0.2
TRH C6-C9	mg/L	<0.2	<0.04	<0.04
Zinc	mg/L	0.11	0.52	0.13

4.8 Summary

Chapter 4 presents SSIX and contributing water geochemical data for the 2007-2011 period. These data, and the patterns present therein, will be further interpreted and discussed in Chapters 5 and 6.

The key summary points presented in this chapter include:

- The SSIX pit is known to exceed water quality guidelines for 6 major ions (Al, SO_4, Fe, Mn, Ni and Cu).
- The 2007 project scope investigation observed the input of major ions from contributing source waters to the SSIX pit.
- The 2007 project scope investigation proved the presence of phytoplankton in the SSIX pit, as well as its contributing bore and surface waters.
- Aerial photos of the SSIX pit, from the past decade, show a potential pattern between water colour and the wet season (brown water colour) or dry season (opaque green, translucent green water colour).
- Aerial photos of the SSIX pit, from the past decade, show no pattern with regard to water colour and volume of water in the pit lake.
- Regular fluctuations can be observed from Mt Tom Price temperature and rainfall data for the past decade (with few major rainfall events – cyclones).
- Fluctuations between calculated and total acidity of the SSIX pit coincide with fluctuations in rainfall.
- Fluctuations in major ion concentrations of the SSIX pit coincide with fluctuations in rainfall.
- Regression analysis failed to establish any strong correlations between physical and climate data and the concentrations of metal ions in pit and bore water.
- Evidence suggests the present contributions of major ion concentrations from the contributing source waters, of the SSIX pit. However, it appears this could be directly dependant on rainfall quantity and leaching times.

5 Analysis of 2012 Samples and Laboratory Results

5.1 Introduction

This chapter presents a summary of data that was collected and analysed in 2012 for the research undertaken as part of this thesis. The interpretation and analyses of data presented throughout this chapter are original to this thesis. The 2012 data supplements the EnviroSys data and archived RTIO files that were presented in Chapter 4. These data enable this project to further investigate specific water geochemistry, biological analysis and acidity characteristics of the SSIX pit and its selected source waters.

The 2012 phytoplankton count analysis, which was performed by Dalcon Environmental, is also reported here in an effort to test the hypothesis that algal growth is causing a weak organic acidity in the SSIX pit.

Chapter 5 also presents the results from the acidity titrations that were completed on each water sample taken in 2012 (from the three sampling periods). In total 9 water samples were analysed for both hot and cold titrations (including 3 replicates of each; 54 titrations total). Titration curve analyses facilitate acidity characterisation of each sample and contribute to the measurements needed to determine total acidity. This is because organic acids commonly have much higher pKa (acid dissociation) values than the dominant mineral acids that typically contribute to AMD, such as aluminium and iron sulphate.

Each component of the data analysis reported in this chapter will be further discussed in Chapter 6 in an effort to combine and compare the results from both Chapters 4 and 5.

5.2 Water geochemistry data

Three separate surface water sampling periods were carried out in 2012 as a direct part of this thesis. Two additional sample collections, made by the RTIO environmental monitoring officer, were also performed in April and July (2012).

Table 5.1 presents the 2012 water geochemistry data in the SSIX pit, throughout seasonal climate changes of 2012. Table 5.1 shows that the highest concentrations of major ions and

metals, and the lowest pH values, occur during the wet season (April). This can also be observed in the Schoeller diagram representation of the major ions (which SSIX exceeds guidelines, Figure 5.1). The wet season concentrations presented are on average 42% higher than the dry season (August). This pattern is similar to the patterning identified in Chapter 4: rainfall events are associated with elevated ionic concentrations. For reference, Figure 5.2 presents the rainfall and temperature changes throughout 2012.

Table 5.1 Reported water geochemistry data by SGS lab for the SSIX pit water samples from 2012 (* water geochemistry data by Cawthron Labs, Nelson).

Sample	Units	03/02/12*	13/04/12	05/07/12	22/08/12	03/12/12
pH	pH units	3.3	2.6	3.1	4.1	3.6
Acidity as $CaCO_3$ (pH=8.3)	mg/L	200	590	300	98	130
Total Dissolved Solids @ 180°C	mg/L	720	2000	1100	730	730
Chemical Oxygen Demand	mg/L	<4	<10	35	91	11
Aluminium, Al	mg/L	25	82	39	14	17
Calcium, Ca	mg/L	40	38	39	27	27
Chloride, Cl	mg/L	82	88	95	97	110
Copper, Cu	mg/L	0.39	1.2	0.44	0.15	0.17
Iron, Fe	mg/L	0.73	130	10	0.67	3.1
Potassium, K	mg/L	7.5	7.1	8.5	7.6	9.7
Magnesium, Mg	mg/L	44	61	66	48	53
Manganese, Mn	mg/L	2.3	3.7	5.1	2.9	3
Sodium, Na	mg/L	38	35	41	35	45
Nickel,Ni	mg/L	0.25	0.72	0.49	0.26	0.27
Zinc, Zn	mg/L	0.14	0.56	0.44	0.24	0.24
Silica, SiO_2	mg/L	28		45	37	40
Sulphate, SO_4	mg/L	430	1400	750	430	410
Nitrate, NO_3	mg/L	1.8	6.3	4.7	4.3	4.1
Phosphorus, P	mg/L	<0.002	-	-	0.03	<0.01
Total Organic Carbon	mg/L	1.2	-	-	-	<0.2
Biological Oxygen Demand (filtered)	mg/L	-	-	-	-	<5

The July and August samples show the expected concentrations for each relative season. However, Figure 5.1 shows the February sample with lower concentrations than expected for a wet season sample. The absence of rainfall before the January (Figure 5.2) could potentially cause low concentrations of major ions seen in the February 2012 water sample. Otherwise there is potential that the low concentrations are due to the extended period of time for the sample to reach Cawthron labs in Nelson, New Zealand, for geochemical analysis. Hence why SGS Perth was used for the remainder of 2012 samples, with delivery within 24 hours.

Prior to December 2012 there is a short period of rainfall in late October 2012. This October rainfall occurred after a long dry period, which might suggest a more permeable/less saturated ground. This rainfall may have been sufficient to cause the increased period of iron concentrations in the December 2012 sample (Figure 5.1).

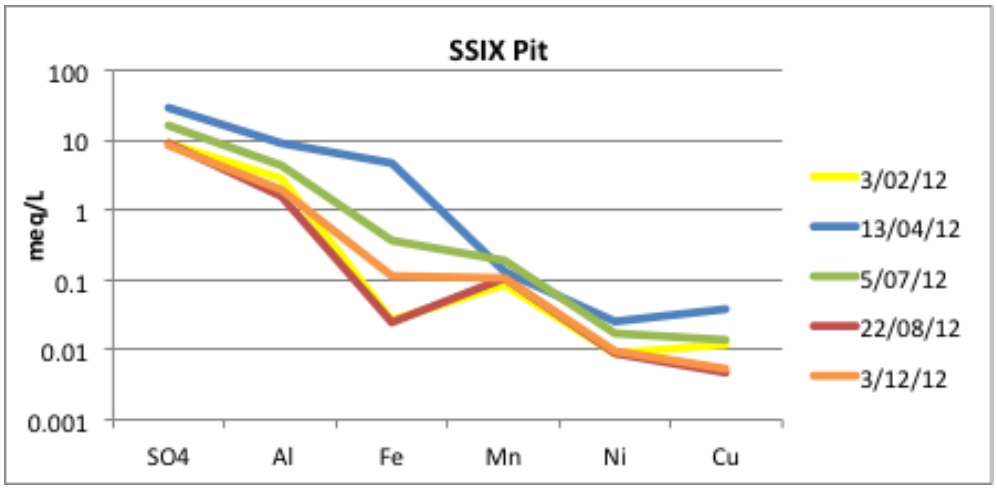


Figure 5.1 Schoeller diagram of SSIX pit water major ion geochemistry for 2012

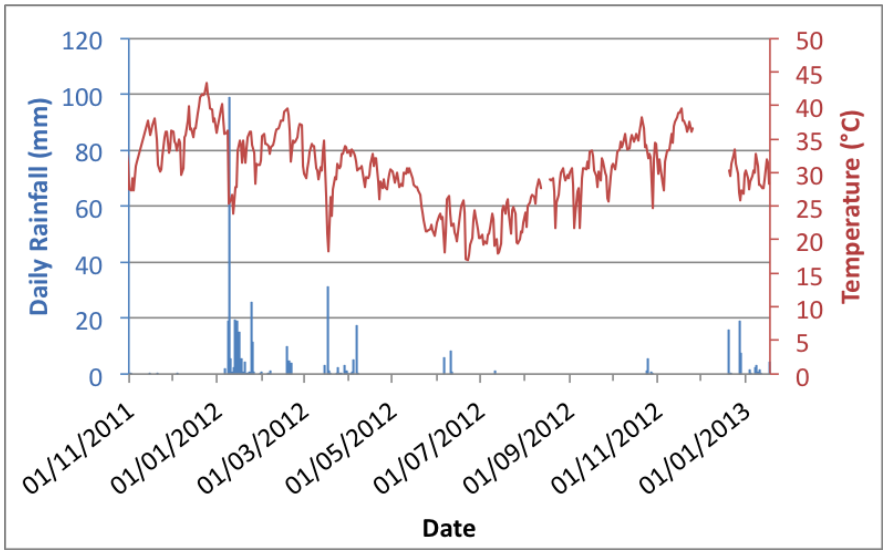


Figure 5.2 Climatograph of Mt Tom Price mine, 2012 rainfall and temperature

The water geochemistry of three SSIX pit contributing water sources; the SEP pit and two selected SEP bores, were also reported on in 2012. Figure 5.3, Figure 5.4 and Figure 5.5 present Schoeller diagram summaries of the major ion concentrations in the source water samples (raw geochemical data is presented in Appendix I). The Schoeller diagram for the SEP pit (Figure 5.3) and the WB06SEP01 bore (Figure 5.4), exhibit a similar decline in major ion concentrations from the wet to the dry season as seen in the SSIX pit water. The SEP pit was exposed to a high period of rainfall in January 2012 (Figure 5.2), which may have resulted in an increase in the concentrations of major ions in SEP water. However, in relation to bore water samples (Figure 5.4 and Figure 5.5), and in comparison with patterns seen in Chapter 4 (Figure 4.14 - 4.16), the water geochemistry of bore WB11SEP02 appears to be less affected by rainfall than bore WB06SEP01. Perhaps WB06SEP01 has a larger transmissivity, causing faster leaching after rainfall and thus higher ion concentrations. WB11SEP02 might experience the delayed effect of leached rainfall (see Section 4.7) and thus would not exhibit as intense a disruption in major ion concentrations.

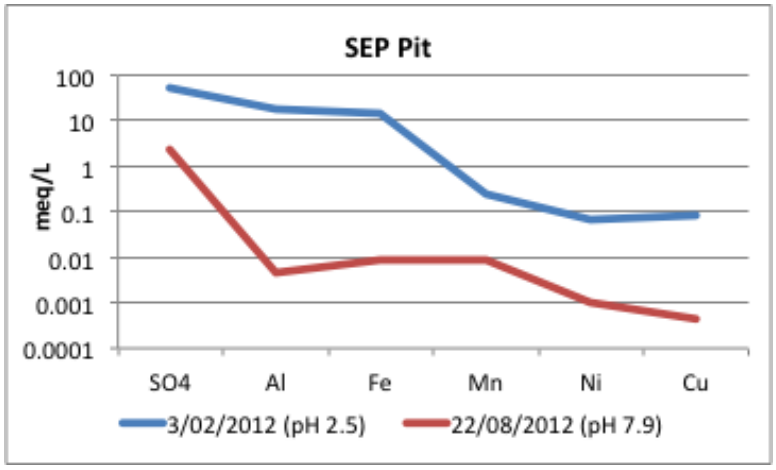


Figure 5.3 Schoeller diagram of the SEP pit water major ion geochemistry for 2012

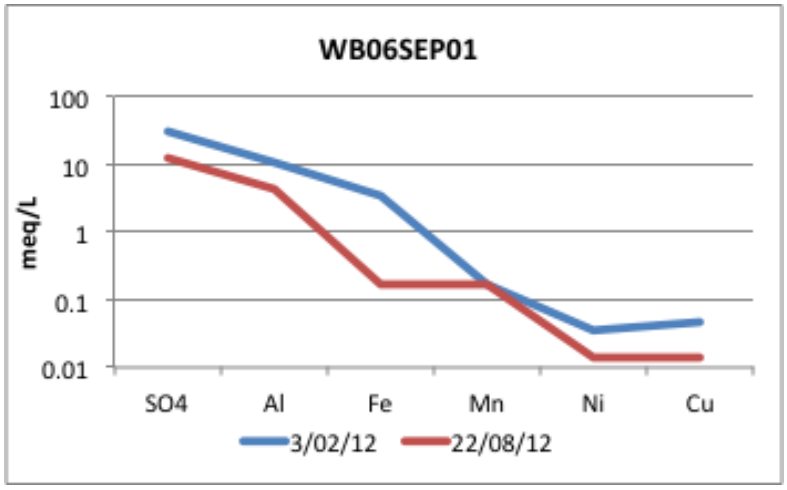


Figure 5.4 Schoeller diagram of the WB06SEP01 bore water major ion geochemistry for 2012

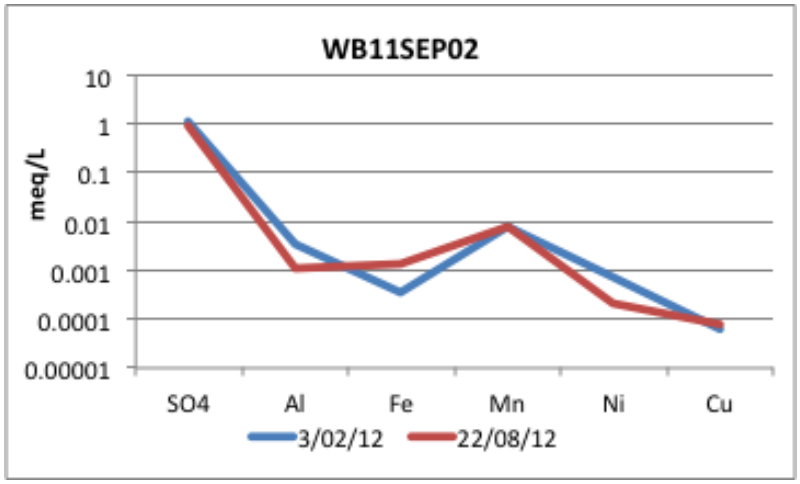


Figure 5.5 Schoeller diagram of the WB11SEP02 bore water major ion geochemistry for 2012

5.3 Phytoplankton Analysis

The 2012 phytoplankton count performed by Dalcon Environmental identified no phytoplankton in the SSIX pit lake samples (Table 5.2). This is in stark contrast to similar analyses made in 2007, when extremely high numbers of phytoplankton in the SSIX pit were observed (Table 4.3). However, a small population of phytoplankton were present in the SEP pit (Table 5.2), which is similar to the 2007 investigation of SEP. The cause of these paradoxical results requires further exploration.

The original phytoplankton count reports (Appendix IV) declare no water colouration in the 2012 SSIX pit, compared to a green water colouration in the 2007 SSIX pit report that contained abundant phytoplankton. However, it should be noted that a translucent green colouration was present in the August 2012 ground photo of the SSIX pit (Figure 4.3). Lack

of algae suggests that this green pit water colouration could be attributed to metal precipitates, particularly those of aluminium and copper sulphates.

No other reporting on biological material in the SSIX pit or contributing water sources was completed in 2012 (such as iron reducing bacteria). Therefore, the low phytoplankton density observed in 2012 suggests that the water geochemistry itself may have been distinctly different between 2007 and 2012.

This possible 'geochemical explanation' will be further explored in Chapter 6, through comparison of the water geochemistry and acidity characteristics present in the SSIX pit water through time.

Table 5.2 Reported densities for phytoplankton count completed by Dalcon Environmental lab

	April		August		December
Phytoplankton Identification	**SEP pit**	**SSIX pit**	**SEP pit**	**SSIX pit**	**SSIX Pit**
Unicellular coccoid alga sp. 001	280 (100)	-	54 (54.55)	-	-
Bacillariophyceae Nitzhia spp.	-	-	45 (45.45)	-	-

5.4 Titrations

Acidity titrations were completed, for each of the three sampling periods in 2012, to characterise the acidity of the SSIX pit and its selected contributing water sources (SEP pit, WB11SEP02 and WB06SEP01). These acidity titrations were used to support the hypothesis that algal growth is disrupting the pit lake acidity, potentially contributing organic/weak acid to the system. Unfortunately because there was no phytoplankton detected in the SSIX pit during 2012, there is no direct evidence to support this hypothesis. However, the use of acidity titrations and acidity characterisation by titration curves is still presented here to inform future research and facilitate exploration of alternative hypotheses capable of explaining the acid inconsistencies characteristic of SSIX.

The figures presented on the following pages display hot and cold titration curve averages for each of the 2012 samples. Data for these curves was determined using the methods described in Section 3.5. To identify the acidic species in each titration sample, the titration curve produced presents the buffer regions of each category of acidic species. The titration curve of samples with lower total acidity (i.e. of a pH ~7), are not displayed here (Appendix III) because they did not produce an informative titration curve.

The difference between each hot and cold titration curves (Figure 5.7 and Figure 5.8) presents the difference in buffering due to increases in oxidised hydrolysable metals consuming more base, in the hot titration curve as well as effects of carbon dioxide (Section 2.6.2).

The distinguishable buffering regions can be categorised into acidic species, with the use of similar titration curve relationships presented in relevant literature. Figure 5.6 (previously explained in Chapter 2; as Figure 2.6), is presented here again for ease of use in the analysis of titration curve results.

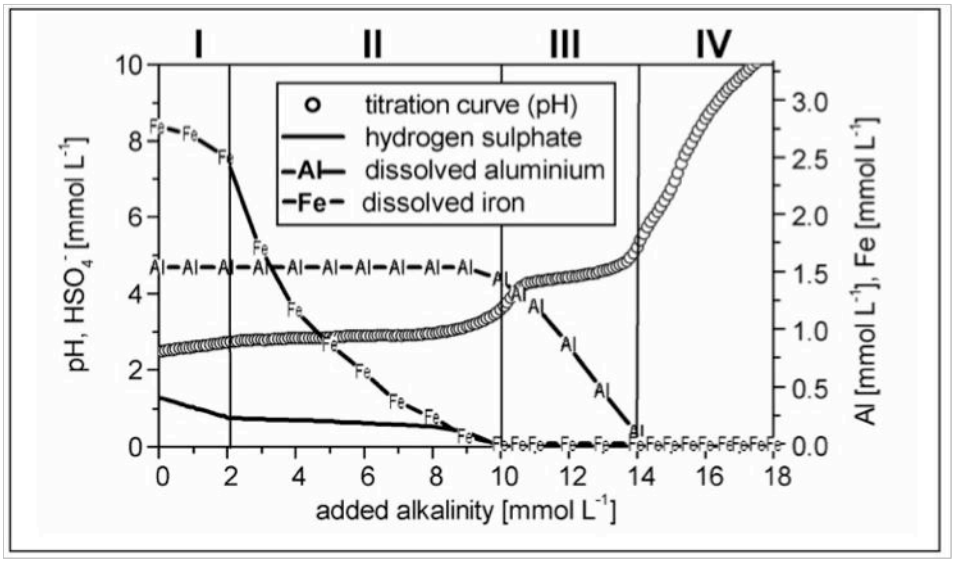


Figure 5.6 An acidity titration example split into its different buffering components, presenting the range each acidic species individually affects the titration curve and buffers out (Totsche et al., 2006).

The buffering regions, as indicated in Figure 5.6, will be identified on each titration curve. This will determine the greatest contributor to acidity of the major ions known to occur in SSIX and its contributing source waters (Al, Fe, Mn, Cu, Zn, SO_4).

Each titration curve (Figure 5.7 and Figure 5.8) displays a lower initial pH value for the hot titration curve (as previously seen in Figure 2.7), due to the additional acidity from the oxidation (hot treatment) of the sample. Following this, it can be seen that the hot titration curve then consumes base additions faster and intersects the cold titration curve just below or above pH 4. However, this observation (for the first part of each figure) shows a very small difference between hot and cold titration curves, which may suggest fewer hydrolysable metals in the AMD water samples as anticipated.

A larger difference between hot and cold titration curves is apparent in the second part of each figure. A larger consumption of the base occurs in the cold titration, due to the delayed oxidation of hydrolysable metals in solution (which have not been previously oxidised like the hot titration treatment).

The first buffer region to be identified is typically the contribution from hydrogen sulphate (Totsche et al., 2006). This is displayed in the grey shaded area of each figure (Figure 5.7 and Figure 5.8). The following buffer region, shaded in red, represents the contribution from iron. When relating these buffer zones to the relevant Schoeller diagram for each sample (Figure 5.3, Figure 5.4, Figure 5.5 and Figure 5.8), it can be seen how the concentration of a major ion can potentially control the amount of related acidic species. This is also weakly reflected in the next buffer region (shaded in green; Figure 5.7 and Figure 5.8), as aluminium declines.

The final un-shaded region, of each titration curve, accounts for the additional metal ion buffers in solution. These metal ion buffers have a delayed oxidation in the cold titration, causing a large buffer region and drifting end point. This region will account for the related acidic species of the remaining ions Mn, Ni and Cu. (present in excess in the SSIX pit and source waters).

Interestingly, the hot titration curve for the August 2012 SSIX sample (Figure 5.8C) displays an initial upwards curve which would usually indicate a weak/organic acid (Figure 3.5). This identification is fitting with the dry season, when an algal bloom would be expected to be present. However, because no algae were identified in the SSIX pit in 2012, this is more likely to be a weak acid as some weak acids are known to produce this pattern. If titration curves could have been produced from the 2007 data (when algae was present) perhaps this zone of buffering weak/organic acid could have been seen. This will be further discussed in Chapter 6.

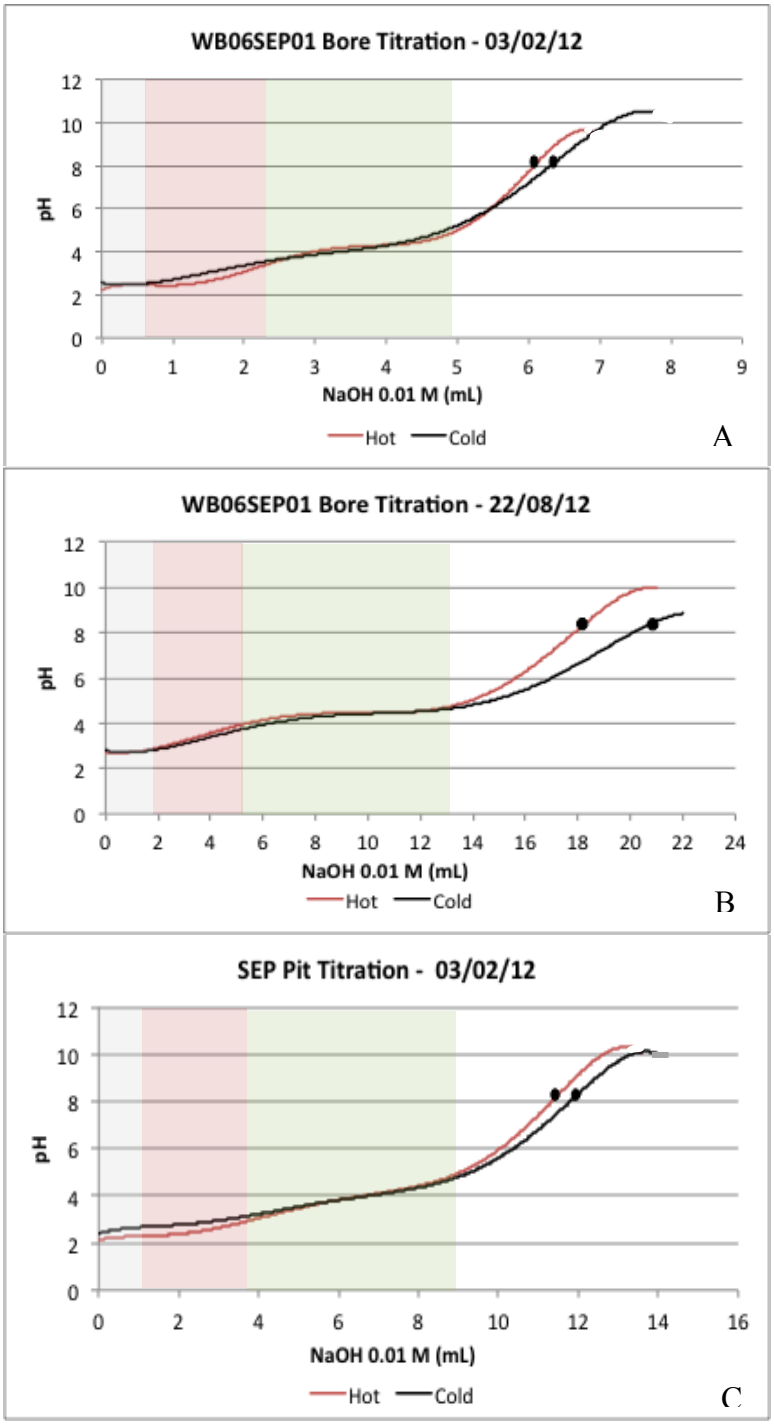


Figure 5.7 The comparison of average hot and cold titration curves for the contributing bore (WB06SEP01) and surface water (SEP pit) inputs to the SSIX pit (Mt Tom Price mine, 2012).

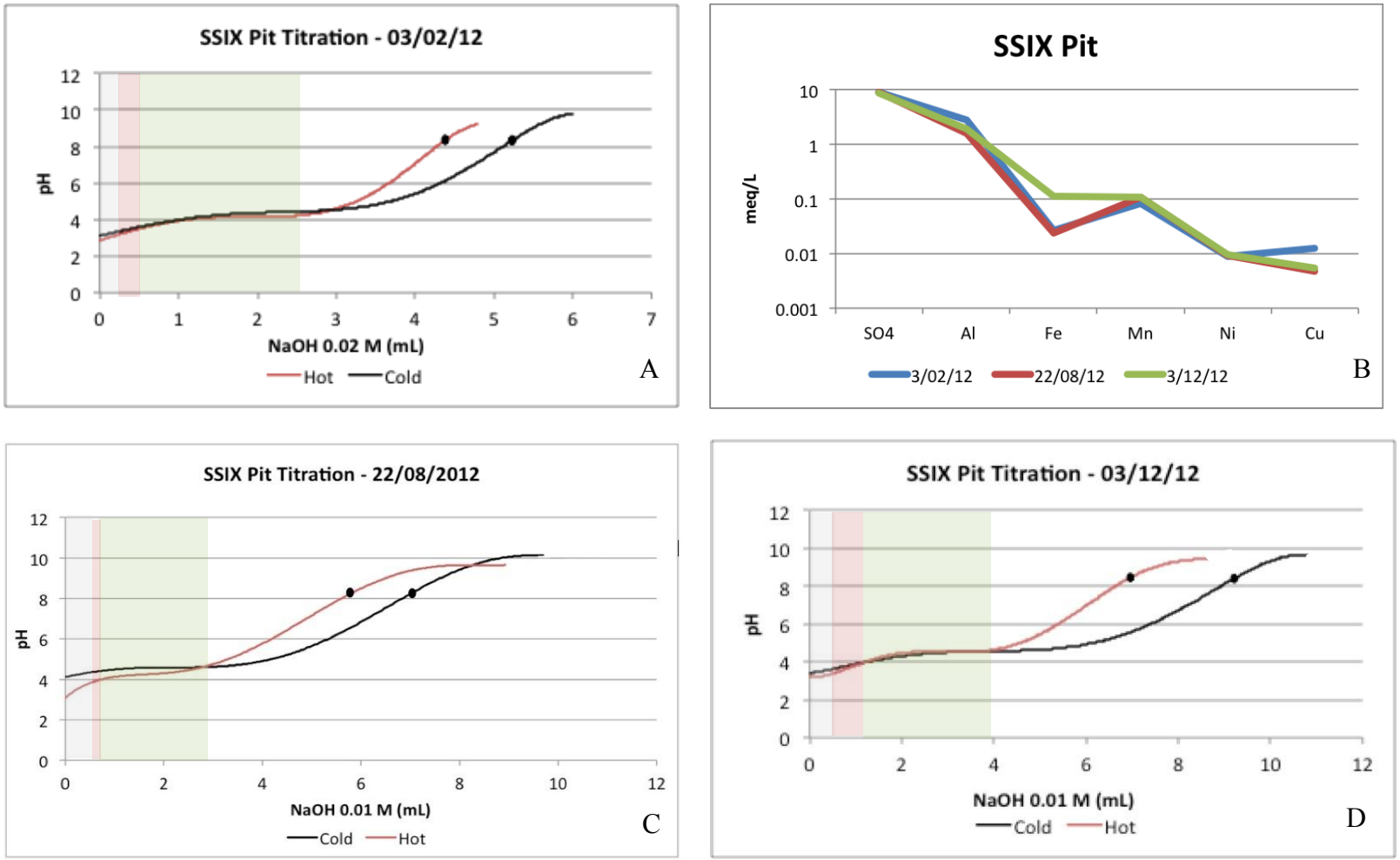


Figure 5.8 The comparison of average hot and cold titration curves for the SSIX pit, alongside the Schoeller diagram of major ion concentrations for the representative dates (Mt Tom Price mine, 2012).

5.5 Total and Calculated Acidity

The geochemical analyses and acidity titrations reported in this chapter were also used to determine calculated and total acidity of each water sample (see Section 3.5.3 for equations). Table 5.3 presents the data that has been acquired from each analysis (ion concentrations and pH from the SGS reports and relative values from titrations) to determine calculated and total acidity. The comparable total acidity determined by SGS hot titrations is also presented at the bottom of Table 5.3.

Total acidity is presented for both the hot and cold acidity titrations, for comparison of technique reliability. Each titration curve shows the chosen titration endpoint of pH 8.3, where the moles of base added equal the moles of acid present (shown by a black dot; Figure 5.7 and Figure 5.8). This end point was used to determine the quantity of base consumed for acidity calculations.

As noted previously, some titration curves remain in the appendices due to the initial neutral pH values producing an insignificant titration curve, with no identifiable acidic species or buffer regions. This was also the case when calculating acidities; a high/neutral pH produced an insignificant acidity value.

Table 5.3 shows a variety of results between calculated and total acidities. The comparison of calculated and total acidities between WB06SEP01 and the SEP pit show no similarities at all for the February 2012 samples. This has since been deduced as an error in the metal concentrations (used for acidity calculation) from SGS laboratory geochemical analysis results, which displayed an unacceptable cation/anion balance (Appendix I). This error will be further discussed in Chapter 6.

Relatively similar acidity values (between calculated and hot total acidity) can be seen from each of the samples for the SSIX pit in February, August and December (2012) and the WB06SEP01 bore in August. A slight difference between calculated and total acidity for the SSIX pit can be seen in the August sample with a calculated acidity of 88 mg/L (as $CaCO_3$ equivalent) and a total acidity of 141 mg/L (as $CaCO_3$ equivalent). However it is noted that the SSIX pit August 2012 total acidity value supplied by SGS, 98 mg/L as $CaCO_3$ equivalent, is more accurate to the calculated acidity. Therefore this has been adopted as the correct value.

The issues that have arisen in this summary table will be further discussed, with relation to the archived data, in Chapter 6.

Table 5.3 Reporting and comparison of total and calculated acidity for samples collected in 2012. (*Actual acidity determined by Cawthron Labs, Nelson)

	3/02/12			22/08/12		3/12/12
	SSIX pit	SEP pit	WB06SEP01	SSIX pit	WB06SEP01	SSIX pit
Calculated Acidity						
Al (mg/L)	25.00	170.00	98.00	14.00	39.00	17.00
Fe (mg/L)	0.73	400.00	95.00	0.67	4.70	3.10
Mn (mg/L)	2.30	6.80	4.80	2.90	4.50	3.00
pH	3.30	2.50	2.50	4.10	2.70	3.60
Calculated Acidity as $CaCO_3$ (mg/L)	**170.09**	**2186.35**	**965.75**	**88.82**	**337.20**	**120.76**
Total Acidity - Hot Titration						
NaOH used (mL)	4.37	11.50	6.15	7.05	18.15	6.86
NaOH normality (N)	0.02	0.01	0.01	0.01	0.01	0.01
H2S04 used (mL)	0.00	0.00	0.00	0.00	0.00	0.00
H2S04 normality (N)	0.00	0.00	0.00	0.00	0.00	0.00
HOT Total Acidity as $CaCO_3$ (mg/L)	**174.80**	**230.00**	**123.00**	**141.00**	**363.00**	**137.20**
Total Acidity - Cold Titration						
NaOH used (mL)	5.22	12.00	6.45	5.87	20.60	9.15
NaOH normality (N)	0.02	0.01	0.01	0.01	0.01	0.01
H2S04 used (mL)	0.00	0.00	0.00	0.00	0.00	0.00
H2S04 normality (N)	0.00	0.00	0.00	0.00	0.00	0.00
COLD Total acidity as $CaCO_3$ (mg/L)	**208.80**	**240.00**	**129.00**	**117.40**	**412.00**	**183.00**
SGS HOT Total Acidity as CaCO3 (mg/L)	200.00*	5700.00	5700.00	98.00	310.00	130.00

Key:	Surface water
	Groundwater

5.6 Summary

Chapter 5 presents the data that was collected during 2012 as a direct outcome of this thesis. The recurrent trend (from the archived data in Chapter 4) of an increase in major ion concentrations associated with periods of heightened rainfall was confirmed.

One of the key results presented in this chapter was the observation that no algal bloom was present in 2012 in the SSIX pit. No large acidity inconsistency occurred, potentially due to the absence of algae. Therefore the 2007 hypothesis that phytoplankton were the sole cause of the acidity inconsistency through generation of weak/organic acid is still likely, but non-conclusive from this thesis.

However, these data have identified some important similarities between 2012 and archived data. For example, despite an absence of algae, the dry season geochemical and titration analyses still produced some evidence comparable to that observed from the 2007 sample

collections, including reduced metal ion concentrations and a (translucent) green colouration of the SSIX pit water.

6 Characterisation of the SSIX pit acidity inconsistency

6.1 Introduction

The primary objective of this thesis was to determine if there was a weak acid presence in the SSIX pit and whether it was caused by the SEP source drainage, or an organic acid from the SSIX algae bloom. This objective assists the characterisation of the acidity inconsistency issue of the SSIX pit. Chapter 6 achieves this objective through discussion of the physical, chemical and biological system interactions that help explain the archival and original data presented in this thesis.

The research undertaken in this thesis intended to test the hypothesis: that biochemical effects associated with the 2007 phytoplankton bloom in the SSIX pit water caused an acidity inconsistency. It was assumed, at the time, that a phytoplankton bloom would in fact occur in 2012, the sample collection period of the thesis research. Unfortunately, this proved to be not the case. As a consequence, the original hypothesis was replaced by a broader set of guiding questions: 1) How did geochemical conditions differ between 2007 and 2012? and, 2) Are these differences compatible with the presence /absence of algae and a recurrent acidity inconsistency?

There are many ways to interpret the currently available SSIX pit water dataset. This chapter presents the interpretations supported by a comparison of the 2007 and 2012 geochemical data in the context provided by supplemental environmental and biological observations. First, the metal ion data are discussed. Second, the occurrence of phytoplankton and third, the acidity inconsistency. Issues associated with predicting future 'algal bloom' events, are also discussed later in the chapter, and the chapter concludes with a series of recommendations aimed at informing future operational responses to phytoplankton blooms in Mt Tom Price surface water bodies.

6.2 Metal ion concentrations

This section discusses the observed covariation between rainfall and major ion concentrations in SSIX pit water (Al, SO_4, Fe, Mn, Ni and Cu). This trend specifically

showed an increase of major ion concentrations during the wet season, which also experiences the maximum annual temperatures. This result contradicts the expected dilution of major ion concentrations with increased rainfall (Davies et al., 2011). However, a review of the literature revealed that similar situations in other AMD producing systems have occurred. In fact, there are several ways to explain these covariant trends: 1) continued chemical weathering of pyritic oxidation products facilitated by water influx (Davies et al., 2011); 2) rainfall induced pressure transmission wherein infiltrating water pushes out older high conductivity groundwater; 3) rapid dissolution of soluble secondary (i.e. evaporite) sulphate minerals or 'first flush' mechanism

Due to the presence of the pyritic Mt McRae black shale and its associated oxidation products on the pit wall, a likely explanation is the 'first flush' mechanism. As stated in Chapter 1, the modelled black MCS exposures cover 18,600 m^2 in the SSIX pit, with the upper extent located at 680 mRL and all exposures below the pre-mining water table (Terrusi, 2013). As described by Davies et al. (2011), 'first flush' events are when rainfall surface runoff flushes down the weathering products from pyrite, which have accumulated over the dry months on the pit wall. The highly soluble mineral products of pyrite weathering (e.g. sulphates) dissolve and discharge into the pit lake (Olıas et al., 2004). Such events cause a lowering in pH and associated increases in metal concentration due to the sensitivity of metal solubility to pH (Gyure et al., 1987). Such events are generally short lived in surface water systems (i.e. streams and rivers) due to dilution, but may have a more prominent signature in pit lakes.

The wet season in the Pilbara is coincident with the period of highest annual temperatures. This hot, wet combination produces maximum annual concentrations of major ions in the SSIX pit. Compared to other climates in the world, where increased concentrations would either occur in the spring during the first rainfall of the year or in the summer months only due to high temperatures causing evaporation of pit lakes and higher conductivities (salinity). The increased temperatures of the Pilbara wet season cause rapid evaporation on the pit walls and increased weathering and oxidation products of metal ion contaminants. As mentioned earlier, these contaminants are then re-dissolved by episodic high rainfall events. Similar

principles, of weathered pit walls and runoff infiltration, contributing to acid water accumulation and pit lake chemistry are highlighted by Johnson and Thornton (1987).

The results in Figure 5.1 showed an increase in iron concentrations in December 2012, after a small rainfall event that occurred in October 2012 (Figure 5.2), contradictory to the seasonal climate. This smaller 'first flush' event illustrates a principle, identified by Olias et al. (2004), that intermediate flow rates generally show the highest concentrations of dissolved constituents, rather than a major rainfall dilution. A larger rainfall period during this colder season (October 2012; where pit wall weathering products are oxidising at a slower rate) may have eventually diluted the system.

The occurrence of the 'first flush' principle in the SSIX pit is therefore the cause of increased major ion concentrations in the wet season. This may also potentially cause phytotoxicity to phytoplankton, which supports the 2007 investigation that phytoplankton are only present during low concentrations of major ions.

6.2.1 Source water to the SSIX pit

The Schoeller diagram results, from samples of contributing boreholes and surface water chemistry (Section 4.7 and Section 5.2), show little evidence of the influence held by major ion concentrations discharged to the SSIX pit water chemistry. However, the 2007 influence from total discharge to SSIX (Table 4.6) and the literature discussed in Section 6.2 present good evidence that rainfall quantity and leaching have a direct impact on the source water system, thus influencing major ion concentrations that are then transported to the SSIX pit.

A similar source water influence on the SSIX pit is seen in relation to phytoplankton presence. The large quantity of phytoplankton seen in the source water in 2007 (Table 4.3), was a major reason for the high phytoplankton count in the SSIX pit. Similarly, the lower presence of phytoplankton in the 2012 source water (Table 5.2; SEP pit) mirrored an absence of phytoplankton in the SSIX pit. The absence of phytoplankton in 2012 resulted in the inability to conclude that source water is 'seeding' algal blooms (which may then evolve along different trajectories depending on pit water chemistry), but this could be investigated in future.

Thus, along with major ion concentrations, contributing source waters have had an influence on the SSIX pit phytoplankton input. Suggesting the reason for phytoplankton absence in 2012 is due to the lower counts observed in the SEP source water. This phytoplankton absence is potentially the reason that no SSIX pit acidity inconsistency was seen in 2012.

6.3 Phytoplankton presence

The observation that SSIX phytoplankton were abundant in 2007 (Table 4.3) but absent in 2012 (Table 5.2), raises the question, "what is/are the control(s) on phytoplankton activity". Clearly, the potential addition of phytoplankton from different source waters is likely a major factor in phytoplankton occurrence in the SSIX pit. However, this section will focus more on the SSIX pit conditions and how they may relate to phytoplankton abundance.

Little is known about phytoplankton communities in acidic pit lake environments and their seasonal colonization (Kalin et al., 2001; Winder et al., 2012). However, one study has shown the development of phytoplankton in an acidic pit lake is associated with light availability, metal concentrations, nutrient levels and pH (Kalin et al., 2001).

Usually phytoplankton blooms are distributed vertically in the water column (Gyure et al., 1987). This can usually be attributed to stratification of light availability and temperature changes. Stratification occurs when heating of water causes colder, denser water to sink to the bottom, creating a hypolimnion layer at the bottom, which is typically anoxic. Stratification is often promoted as an option for containment of AMD effects in pit lakes, to contain metal and acidic contaminants in the anoxic hypolimnion (Brunt, 2009). Stratification is strongest in the summer months when solar radiation creates a strong temperature contrast in the lake. During colder months the contrast decreases as water temperature drops, allowing mixing of waters. Wind also reduces stratification by mixing of the water column (Brunt, 2009). However, a DYRESM (Dynamic Reservoir Simulation Model) study on the stratification of the SEP pit lake shows that the pit walls produce a 90% wind sheltering effect (Oldham and Bibhash, 2012). This aids a strong stratification in the SEP pit, a viable analog to the SSIX pit.

The SSIX pit appears to have consistent light availability due to the opencast nature of the pit, with little shade. This could be suggested as a negative habitat, due to potential increase of water temperature from solar heating. However, archived climate data displays consistent fluctuations in water temperature relative to air temperature (Figure 4.5), albeit potentially excluding the hypolimnion. This range of temperature fluctuations would produce suitable conditions for phytoplankton activity, with the optimal growth temperatures in the dry season (between 25°C and 40°C).

However, vertical distribution of phytoplankton is not always solely due to light and temperature. Motile phytoplankton may also position themselves closer to anoxic sediments at the bottom of a lake because of more rapid nutrient releases (such as phosphate) from sediments, which may be limited elsewhere in the water column. Positioning themselves at the bottom of the lake does, however, make them subject to reduced temperatures and decreased light availability, which may reduce primary production (Gyure et al., 1987).

Phytoplankton situated close to the anoxic sediments at the bottom also have the potential to be affected by sulphide toxicity through settling of sediments with bound sulphides (Gyure et al., 1987). There is a high potential for this to occur in the SSIX pit, due to the high concentrations of major ions in the wet season, precipitating out and settling on the lake bottom in the dry season.

Light and temperature can also cause direct and indirect effects on resource availability in the aquatic system (Winder et al., 2012). Phytoplankton blooms can supply a large amount of energy to ecosystem functions. Trophic interactions such as zooplankton predation therefore provide another potential reduction in phytoplankton presence (Winder et al., 2012).

In terms of phytoplankton presence related to water chemistry (metal concentrations and nutrients), Nixdorf et al. (1998) explains how it is water chemistry that depicts phytoplankton species diversity, but nutrient levels which determine biomass. As found in other acidic environments where the diversity of algae in acidic lakes is low (Gyure et al., 1987). When water quality improves, there is the tendency for changes in community structure; as species richness increases and competition occurs (Kalin et al., 2001).

As mentioned previously, contributions of phytoplankton from source water is a major factor in its presence. Contribution of nutrients from source waters further contributes to successful phytoplankton growth. Table 4.1 shows the individual water chemistry contributions of source waters in 2007, with relatively high concentrations of nitrate (averaging at 14.8 mg/L). Table 6.1 shows the comparison of nutrient contributions from August 2012 data. Overall a much smaller contribution of nitrate is observed, compared to 2007 data. This is indicative of the lower phytoplankton growth also present in 2012. Table 6.1 also shows that there was less phosphorus, but more nitrate, in SSIX pit water in 2007 than in 2012. The simplest way to explain these compositional changes, given the observed differences in phytoplankton abundance between 2007 and 2012, is to assume that phosphorus has been taken up by the abundant phytoplankton in 2007, and the elevated nitrate concentrations are due to perturbations to the local nitrogen-cycle associated with the algal bloom and its biogeochemical flow on effects.

The following section will further discuss the relationship held between metal concentrations and phytoplankton presence.

Table 6.1 Concentrations of TDS, P and NO_3 in the SSIX pit during August 2007 and August 2012, along with concentrations from the 2012 source waters (red). As reported by SGS Laboratories (see Appendix I and II for full reports)

	31/08/2007	22/08/2012			
	SSIX Pit	**SSIX Pit**	**WB11SEP02**	**WB06SEP01**	**SEP Pit**
TDS	560 mg/L	730 mg/L	400 mg/L	950 mg/L	500 mg/L
Phosphorus, P	<0.1 mg/L	0.03 mg/L	0.02 mg/L	0.10 mg/L	0.03 mg/L
Nitrate, NO_3	18 mg/L	4.3 mg/L	3.9 mg/L	6.0 mg/L	3.2 mg/L

6.3.1 Metal toxicity to Phytoplankton

As previously mentioned phytoplankton presence appears to be during periods of decreased major ion (metal) concentrations. Trends of assumed phytoplankton presence in the SSIX pit has been categorised as an opaque green (OG) water colouration. When closely identifying other trends that occur in the SSIX pit related to increased rainfall and major ion concentrations, it can be seen that phytoplankton

growth generally occurs when these conditions do not exist, in the dry season. Absence of phytoplankton in the wet season indicates a potential toxicity caused by major ion concentrations, a metal phytotoxicity. Figure 6.1 shows that, apart from Fe, there are generally lower concentrations of phytotoxic metals such as Al, Ni and Cu in the 2007 August sample, when phytoplankton are present (compared to 2012), indicating a potential for lower metal toxicity to phytoplankton growth. Table 6.1 also shows the difference in water chemistry between the two years with the lower TDS in 2007 (see appendix for full SGS reports).

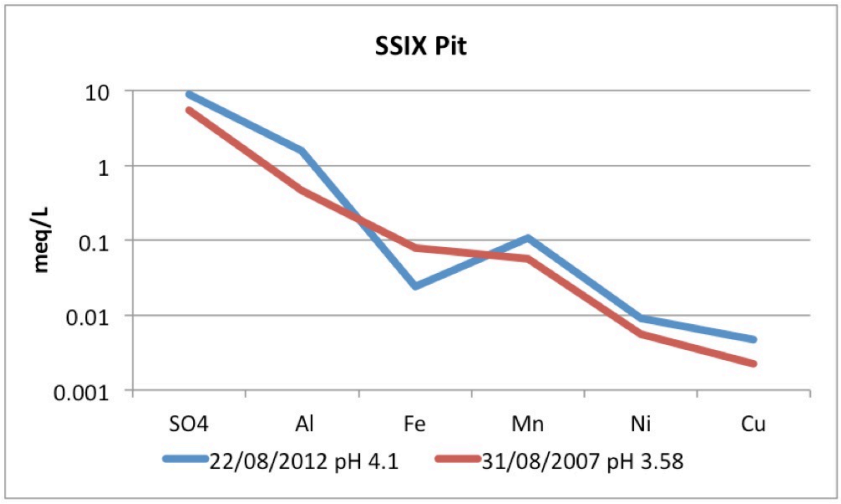


Figure 6.1 Schoeller diagram of the SSIX pit major ion chemistry for August 2007 and August 2012.

Metals that provide essential nutrients to organisms can also potentially be toxic at higher concentrations (Mann et al., 2002). Copper is an example of this, whereby it provides a component of respiratory proteins and oxidases, yet free copper (Cu^{2+}) has been shown to reduce cell division rates of phytoplankton in culture and decrease photosynthetic rates at high concentrations in natural environments (Mann et al., 2002). Table 6.2 shows the differing concentrations of copper in the SSIX pit, related to presence or absence of phytoplankton (and other potentially phytotoxic geochemical characteristics). Mann et al. (2002) states that cyanobacteria are one of the most sensitive species to copper toxicity in the laboratory. This is most likely due to the ancestral beginnings of cyanobacteria and their evolution in ancient sulphidic oceans where Cu, Zn, and Cd were significantly less available than Fe, Ni, Co and Mg (Baptista and Vasconcelos, 2006; Mann et al., 2002). Both Cu and Cd occur at much higher concentrations today and Cu, Fe, Ni and Zn are essential elements to

cyanobacteria cellular metabolism. Copper can also interfere with the uptake of other essential trace metals. However complexes of copper can reduce the amount of free copper in a solution, thus reducing the negative effects which can occur (Mann et al., 2002). Both of these contradicting elements of copper toxicity are highly likely to be present in the SSIX pit, with phytoplankton growth present during reduced concentrations of copper (Table 6.2), as well as the potential for copper speciation (due to the many dissolved constituents).

Table 6.2. This table shows the pit water colour and geochemical properties related to phytoplankton presence or absence. NB. At Tom Price samples are not filtered in the field so the measured dissolved concentration in the water may include precipitates (as the samples is acidified immediately after collection re-dissolving the metal precipitates).

Date	31/08/2007	13/04/2012	22/08/2012	03/12/2012
Colour	Opaque green	Brown	Translucent green	Translucent green
Phytoplankton	Present	Absent	Absent	Absent
Cu (mg/L)	0.07	1.2	0.15	0.17
Al (mg/L)	4.1	82	14	17
Fe (mg/L)	1.6	130	0.67	3.1
SO_4 (mg/L)	260	1400	430	410
TDS (mg/L)	560	2000	730	730
TSS (mg/L)	14	34	11	13
pH	3.6	2.6	4.1	3.5

Cyanobacteria can conduct metal sequestration in an aquatic environment and affect metal speciation (Baptista and Vasconcelos, 2006). The 2007 phytoplankton bloom may have sequestered metal ions, facilitating further phytoplankton growth. The high surface to volume ratio of cyanobacteria cells is usually an advantage for uptake of limited trace elements. However, this can be disadvantageous when trace elements are present in potentially toxic concentrations, compared to large eukaryotic cells which tend to be more resistant to high copper concentrations (Mann et al., 2002). Once inside the cell, the toxic metal cations tend to bind to thiol groups that inhibit enzyme activity or interfere with physiological functions of other cations (Baptista and

Vasconcelos, 2006). Concentrations as low as 1μM of Cu, Zn and Cd are known to cause a stress response by cyanobacteria, in the study completed by Baptista and Vasconcelos (2006).

Other variables, related to phytoplankton presence, which may be indirectly affected by metal concentrations include nutrient limitation and light availability (Mann et al., 2002). Phosphorus nutrient levels have been known to decrease due to co-precipitation with iron (Kalin et al., 2001). Light availability can increase copper toxicity (Mann et al., 2002). Light availability can also be decreased due to increased turbidity, from high concentrations of metal precipitates restricting light (TSS; Kalin et al., 2001).

With regard to all presented here, it is important to note again that physical and chemical water characteristics influence phytoplankton presence and species composition, but nutrient levels determine biomass.

6.3.2 Pit water colour

An important aspect of the 2007 investigation was the initial identification of algae, in the SSIX pit, from the green colouration of the water. However this suggestion needed to be tested because water colour can be influenced by many factors, not just phytoplankton. Dominating particulate matter, such as dissolved humic substances, suspended sediments (precipitates) and a range of soluble salts can also produce a wide range of pit water colours (Boyd and Tucker, 1998).

It was originally thought that the green colouration of the SSIX pit water in 2007 was solely due to phytoplankton presence. However, subsequent investigation, in 2012, demonstrated that a similar green colouration also occurred during an absence of phytoplankton. Three colour categories were thus determined from the archived aerial photos of the SSIX pit.

This revised colouration classification is consistent with both the biological and geochemical datasets:

- Brown: indicating the presence of metal precipitates, such as iron (i.e. high TSS).
- Translucent green: indicating further precipitates with pH increase, such as aluminium and copper sulphates.

- Opaque green: suggesting presence of phytoplankton bloom.

Previous studies, in pond aquaculture management, have also suggested the use of colour categories to identify algal blooms, much like how colour charts are used for soil classifications (Boyd and Tucker, 1998). This would be a useful measure of algal presence in preliminary studies. Specific types of phytoplankton communities produce characteristic colours (ranging from reds, yellows and greens). However as of yet, standard methods for assessing colour have not been developed.

Annual aerial photos of the SSIX pit show a pattern between water colour and the wet season (brown water colour) and dry season (opaque green, translucent green water colour). Phytoplankton identified in the SSIX pit are blue-green algae, which are known to produce a blue-green water colour much like the opaque green category. The brown colouration of pit water in the wet season indicates presence of metal precipitate. Metals can precipitate out in a range of colours. Water colour typically affected by AMD starts as orange, red or yellow-brown during the presence of iron precipitate at a pH above 3.5. As the pH continues to rise, during the seasonal changes toward the dry season, additional metals precipitate out (whilst the brown iron precipitate settles to the lake bottom). For example, aluminium produces a white precipitate (Fripp et al., 2000). Figure 6.2 presents a potential example of this white precipitate occurrence in the December 2012 photograph of the SSIX pit. Other white precipitates typically seen in AMD include anhydrite (anhydrous calcium sulphate).

Following the white aluminium precipitate a blue-green colour can occur from the presence of soluble copper sulphate and further aluminium and iron salts (Buckby et al., 2003; Fripp et al., 2000). It is most likely that this is the cause of the translucent green colour seen in the SSIX pit, when phytoplankton is absent (Figure 6.2 and Figure 6.3). Precipitates have the potential to negatively affect microorganism or algal growth by clogging benthic habitats.

Table 6.2 shows the concentrations of Fe, Al, Cu and SO_4 in relation to pit water colour and phytoplankton presence. Primarily, low concentrations of metals during opaque green colouration and phytoplankton presence and higher concentrations of metals during translucent green colouration and especially during brown colouration, when phytoplankton were absent. At Tom Price, samples are not filtered in the field so the measured dissolved concentration in the water may include precipitates (as the

samples are acidified immediately after collection re-dissolving the metal precipitates).

It should also be noted that Fe^{2+} can also produce a green colour, usually referred to as green rust (Bernal et al., 1959). However this occurrence is only found in anoxic environments, it is noted that there is potential for an anoxic environment to be present on the SSIX pit lake bottom where settlement of Fe^{2+} green rust could display an additional green colour.

Figure 6.2 Evidence of white precipitate (aluminium precipitate and anhydrite) and blue-green precipitate (aluminium and copper sulphates) in the SSIX pit water. Mt Tom Price mine 03/12/12.

Figure 6.3 Evidence of blue-green precipitate (aluminium and copper precipitates) in the SSIX pit water. Mt Tom Price mine 22/08/12.

The possible mechanisms discussed above can be evaluated through comparison with other pit lake water colours at Mt Tom Price mine. For example, the North Deposit Pit displays a very green water colour and (relatively) highly vegetated surroundings (Figure 6.4). Whereas, the SEP pit lake displays a reddish-brown water colour (Figure 6.5). From chemical data collected of the North Deposit in December 2012 and the SEP pit in January 2013, is it apparent that the metal ion concentrations are very low in the North Deposit and relatively very high in the SEP pit. Figure 6.6 compares the water chemistry for these differing pit water colour scenarios. The 2007 SSIX pit as well as the 2012 data are also presented. Figure 6.6 suggests metal phytotoxicity and provides further rationale for the pit water colour categories developed in this thesis.

Figure 6.4 Green pit water colouration and vegetation present in the North Deposit. Mt Tom Price mine, 31/01/2013.

Figure 6.5 Reddish-brown pit water colouration in the SEP pit. Mt Tom Price mine, 31/01/2013.

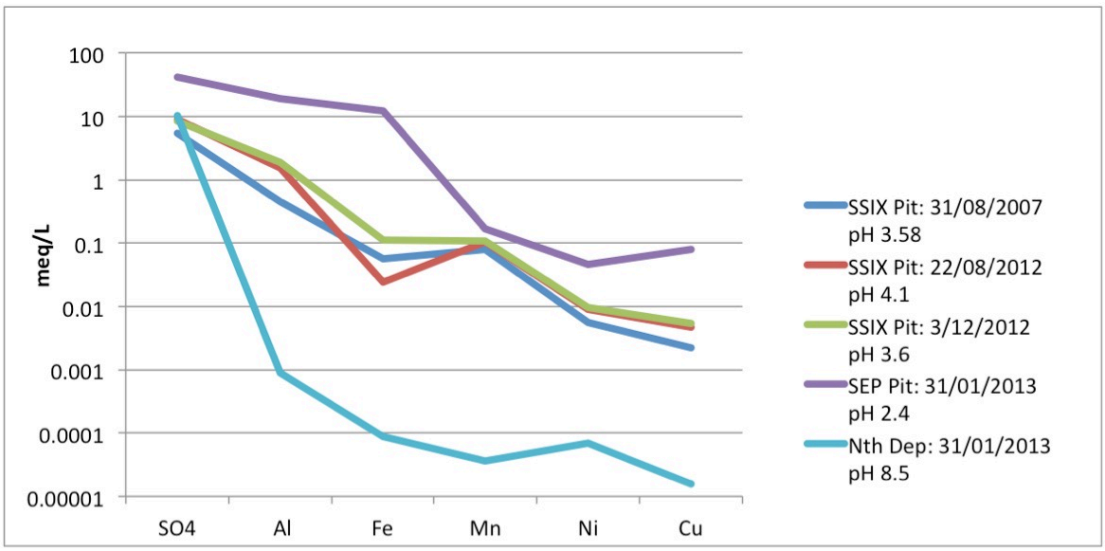


Figure 6.6 Schoeller diagram comparison of major ion concentrations from the SSIX pit, SEP pit and the North Deposit of Mt Tom Price mine.

Figure 6.6 also provides a good example that the solubility of Fe and Fe-oxides are highly pH dependent. This is justified by the lower iron concentration in the SSIX pit August 2012 sample compared to the December 2012 SSIX pit sample, which has a lower pH.

As an alternative to relatively lab intensive pit water colour monitoring and classification, multiband satellite imagery may be a more efficient and perhaps more instructive method for conclusive reasoning of pit water colour. This type of satellite imagery facilitates identification of vegetation (and processes such as photosynthesis), which adsorbs red (600-700nm) and near infrared (700–1100nm) wavelengths of the electromagnetic spectrum (Markert et al., 2003). This method can also be used to determine what kinds of minerals are present. Furthermore, such approaches could also be used to determine when phytoplankton are present in pit waters.

6.4 Acidity inconsistency

The primary objective of this thesis was to characterise the nature of acidity produced in the presence of algae/phytoplankton in the SSIX pit water. This goal was hindered by the absence of phytoplankton during the thesis study period. However, an acidity characterisation was still completed the results of which were extremely useful for determining the magnitude and variability in acid inconsistency between years – both

with and without phytoplankton. It is hoped that these results will continue to benefit and inform RTIO's operations at Mt Tom Price in the future.

6.4.1 Titrations

The pH titration curves displayed in Section 5.4 highlight the pH buffering zones of metal ions precipitating out of solution as hydroxides. The pattern of pH buffering in Figures 5.7 and 5.8 show consistent results of iron precipitation occurring over the pH range pH 2.5 - 4, aluminium precipitation over pH 3.5 - 5, followed by remaining precipitates such as copper and manganese. Each of these precipitation behaviours have been produced as expected and can be compared to literature (Lee et al., 2002). It is generally accepted that Mn precipitates at pH ~ 8, thus it is unlikely Mn precipitate will be naturally present in the SSIX pit due to the lower pH usually present.

These titration curves provide a laboratory representation of the pH buffering by metals, as pH increases across seasonal changes in the SSIX pit. It could be argued, with the previous discussion of pit water colour, that the SSIX pit does not often reach the required pH (>5) during the presence of translucent green pit colour (requiring Al and Cu precipitates). My opinion is that some sections of the lake experience a higher pH than others, much like a horizontal pH stratification. Therefore, resulting in a translucent green colouration in only certain spots of the SSIX pit lake. Figure 6.7 displays this pH horizontal stratification, with differing coloured precipitates in separate zones.

Figure 6.7 Identification of separate colour category zones in the Section Six pit, dependent on the metal precipitate present at differing pH zones from horizontal stratification. 1) Brown; Iron precipitate. 2) Translucent green; dominated by white aluminium precipitate. 3) Translucent green; dominated by blue-green aluminium and copper precipitate. (Section Six pit, Mt Tom Price mine, December 2012).

6.4.2 Total and calculated acidity

This thesis applies the method of comparison of total (acidity from hot titration) and calculated (acidity from metal ion concentrations) acidity values to provide an evaluation of the completeness and quality of analytical results. This method has also been completed by multiple other studies (Hedin, 2006; Kirby and Cravotta, 2005). This thesis also uses acidity comparisons to identify presence and influence of potential weak/organic acidity, which may be identifiable in the total acidity but not the calculated acidity (due to its dependence on metal ion concentrations). This rare use of acidity values was first addressed in the 2007 SSIX pit investigation, due to the large inconsistency in the two acidity values. This suggested the idea that an organic acidity must be present in the total acidity (280 mg/L equivalent $CaCO_3$) due to the algal presence, which was thus unaccountable in the comparative calculated acidity (45 mg/L equivalent $CaCO_3$). However, no titration curve analyses were completed in 2007 to conclude this presence of organic acidity. This conclusion was also unfortunately unachievable by this thesis, due to the absence of phytoplankton (and any potential organic acidity) in the 2012 titratable samples.

The study by Hedin (2006) states that in order to produce viable acidity comparisons standard procedures must be followed to reduce error in water sampling and analysis. It is suggested that to make acidity comparisons as accurate as possible, samples should be collected without suspended solids and pH and alkalinity should be measured in the field or after immediate delivery to laboratory. When these conditions are followed it is generally accepted possible to identify suspect data or laboratory analysis. On average it should be possible to produce calculated acidity within 5% of the total acidity of a sample (Hedin, 2006).

The practices that RTIO apply to sampling and analyses are sufficient to those described above, hence the query of any unexpected acidity inconsistencies in the samples presented in this thesis. (Hedin, 2006). The results of total and calculated acidity (Table 5.3), showed large irregularities for the SEP pit and the WB06SEP01 bore (February 2012 samples). Thus, this is due to an error during SGS laboratory chemical analysis, identified from the unacceptable cation/anion balance (see original SGS report in Appendix I). This imbalance accounts for the large values reported for the metal concentrations used for the acidity value calculations (Table 5.3).

From the four viable results in 2012 (excluding the samples WB06SEP01 and SEP pit of February, due to the unacceptable cation/anion balance; Table 5.3), an average acidity deviation of 14% is produced. This weakly compares to the recommended 5% deviation. However, 14% could still be described as a positive outcome due to the minimal data set of 4 samples used in this thesis, compared to large data sets used in comparative literature (Hedin, 2006; Kirby and Cravotta, 2005). No extreme acidity inconsistency (alike that of August 2007) was experienced in 2012. A slight inconsistency can be seen in the August 2012 values (calculated acidity; 88 mg/L equivalent $CaCO_3$, versus hot titration total acidity; 141 mg/L equivalent $CaCO_3$), however this inconsistency is concluded to be an error in my titration method (most likely an error in the NaOH titrant standardisation). The more accurate SGS total acidity (98 mg/L equivalent $CaCO_3$) was adopted as the correct value.

The absence of acidity inconsistency in 2012, alongside absence of phytoplankton, cannot completely justify the hypothesis of 2007 that phytoplankton produce organic acids disrupting acidity value comparisons. The following will describe other reasons that may account for non-organic sample disruptions for cause of acidity inconsistencies.

Comparisons between total acidity (by hot titration) and calculated acidity, by Kirby and Cravotta (2005), determined that titration samples typically over pH 4.5 produced an acidity inconsistency. This was due to alkalinity present in the samples, which is similar to what was seen in this thesis with samples of a neutral pH (Appendix III). This acidity inconsistency, due to higher alkalinity in the water sample, could also potentially justify some acidity inconsistency in the SSIX pit. The comparison of SSIX pit acidity values (Figure 4.6 and 4.7) during periods of increased rainfall displayed less inconsistency. Perhaps when rainfall is absent and metal ion concentrations decrease (thus high pH), a larger proportion of alkalinity is present in the sample causing the acidity inconsistency.

Phytoplankton metal sequestration may also be a concern to acidity inconsistencies in the SSIX pit. As mentioned in Section 6.3.1, phytoplankton has the ability to sequester metal concentrations from the water. There is potential that sequestration would disrupt the metal concentrations that are used for acidity calculations, causing inconsistency between acidity values.

Any delay in courier from sampling to geochemical analysis could potential alter the concentrations or species of dissolved constituents in the sample. This was potentially observed in the February 2012 sample, sent from Perth to Cawthron laboratory in Nelson, which required an extended period of time to courier and may be resultant in the lower-than-expected-concentrations of major ions in solution. The same delay in courier (compared to courier within 24 hours to SGS Perth for geochemical analysis) was also experienced for samples traveling to Canterbury University from Perth, for titration analysis. This delay could have potentially caused inconsistencies between the calculated acidity (determined from SGS Perth geochemical reported values) and the total titratable acidity (determined at Canterbury University). However the pH, which was recorded before titration, always matched that which was recorded within 24 hours (since sampling) by SGS.

It is also relevant to note here that, CO_2 is known to cause incorrect end points in cold titration samples and perhaps was observed in some of the irregular acidities in bore water samples, such as WB06SEP01. This would effect bore water samples more than surface water, due higher concentrations of CO_2 being present in bore/groundwater, unable to be released to the atmosphere before sampling.

Two more non-organic causes for acidity inconsistency are also noted here for theoretical purpose, but do not apply to the acidity inconsistency observed in this thesis. First, the potentially that filtered and non-filtered samples may occur for different geochemical or titration analyses. If a filtered sample is used for geochemical analysis then the metal ions that may have bonded to fine colloidal clay complexes in solution, may be excluded from analysis. This could then be inconsistent with a non-filtered sample used for hot acidity titration analysis, which would thus include all metal ion species in solution. As mentioned previously, this is not the case for Mt Tom Price samples, which are not filtered in the field so the measured dissolved concentration in the water may include precipitates (as the samples are acidified immediately after collection re-dissolving the metal precipitates).

Second, the calculation method used to equate calculated acidity could potentially be seen to cause error in comparison to total acidities. Green et al. (2006) demonstrates a robust method, which utilises a speciation model to determine concentrations for the entire class of acidic species in solution, rather than the method used by this thesis of only equating Fe, Al and Mn concentrations. However it is acknowledged here that the method used by this thesis is sufficient, due to entire speciation not accounting for more than another 1-2 mg/L $CaCO_3$ acidity (Green, 2013).

6.5 Recommendations for removal of acidity inconsistency

A lack of paired observations of geochemical analysis and laboratory proven algal presence, either in archived data or observations made during this study, caused difficulty when conclusively analysing the acidity inconsistency issue in the SSIX pit and providing recommendations for RTIO. However, if the phytoplankton bloom does occur in excess again this thesis has determined that it will most likely be attributed to a combination of source water contribution of phytoplankton, nutrients and habitat conditions for primary productivity.

In the occurrence of another algal bloom in the SSIX pit, which may cause a large inconsistency with total and calculated acidity, it is recommended that the following sampling and analytical methodology is undertaken:

- Higher temporal resolution of investigation and analyses completed in the SSIX pit.
- Laboratory analysis of phytoplankton presence.
- Chemical analysis of the pit water for an accurate calculated acidity.
- Acidity titration curve analysis of water samples, for identification of potential organic acidity and its behaviour contributing to the SSIX pit acidity characteristics [highly recommended].

If the algal/phytoplankton bloom causes a negative impact on the surrounding environments or processes of the acid water treatment plant, some possibilities for recommended removal have been researched.

Biocides are anionic surfactants such as sodium dodecyl sulphate (SDS). Biocides are a source control regularly used on AMD, as they inhibit or destroy colonies of iron and sulphur oxidising bacteria (Motsi, 2010). SDS is highly toxic to this group of microorganisms. These biocides could potentially be used to destroy similar bacteria, such as the cyanobacteria (phytoplankton) in the SSIX pit. Experiments shows that biocides are only useful for short-term control and therefore will require repeated applications. However, this is usually only relevant in running streams where the chemicals are washed away (Johnson and Hallberg, 2005; Motsi, 2010).

The use of algaecides, such as copper sulphate, to control cyanobacteria growth in water supplies is also a common procedure. In fact, AMD-generated copper sulphate may have inhibited phytoplankton growth in 2012. However, mutations of Cu-resistant cells have arisen, which can also provide overall metal tolerance to a certain extent (Baptista and Vasconcelos, 2006). Despite this fact, it is still a very achievable treatment to remove or reduce a seasonal bloom of phytoplankton. Application of algaecide is administered by spraying the surfactant on the pit lake surface. However, at Mt Tom Price mine the application could be altered to also be administered in pipes and pumps in-between the SEP, SSIX and AWTP. This could also help with reduction of biofouling.

It is also noted here that the addition of $CuSO_4$ algaecides to a water body may cause added acidity. This is due to the readily soluble substance producing not only Cu^{2+} (for toxic use on phytoplankton) but also SO_4^{2-}. The SO_4^{2-} will add acidity to the

water body, as discussed in Chapter 2. However small this increase may be, it should be known and noted for further AWTP neutralisation.

6.6 Summary

This chapter has discussed the results of this thesis and their relevance to the scenario in the SSIX pit of Mt Tom Price mine. A large number of direct and indirect effects play a role in the complicated acidity inconsistency issue (controlled by physical, geochemical and biological characteristics), which this discussion has highlighted and compared to relevant literature.

The comparison of observations made on 2012 water samples with those of 2007 samples, have indicated that the hypothesis produced from the investigation in 2007 is not solely conclusive.

- Green pit water colour is not solely due to phytoplankton presence. Precipitation of metal ions in solution can also cause a translucent green colour.
- Phytoplankton presence is most likely the key cause of acidity inconsistences in the SSIX pit (through potential production of organic acidity) but cannot be fully accounted for due to phytoplankton absence in this 2012 thesis investigation. Thus, reasoning has been additionally provided for other non-organic occurrences of acidity inconsistency.

It is recommended that if similar events surrounding phytoplankton bloom and acidity inconsistency in the SSIX pit occur, alike 2007, the acidity characterisation methods developed in this study along with the removal methods proposed be used by RTIO to investigate the potential of organic acidity further.

7 Conclusions

7.1 Project Summary

This study was undertaken to determine the cause of acidity inconsistency identified in the SSIX pit lake at Mt Tom Price Mine, Pilbara, WA. The 2007 investigation, which highlighted the inconsistency between calculated (determined by metal ion concentrations; 45 mg/L as $CaCO_3$) and total acidity (determined by hot acidity titration; 280 mg/L as $CaCO_3$), also reported a green colouration in the SSIX pit lake; later confirmed as the presence of an algal growth. It was hypothesised that the algae was potentially forming a weak organic acid that was not detected in the calculated acidity.

To test this hypothesis, this thesis undertook another site-specific investigation into the SSIX pit in 2012. However, the absence of any algal growth in 2012 made it difficult for this thesis to conclusively test the 2007 hypothesis directly. Instead, this thesis was able to consider the question: "what observations and measurements differ between water sampled in 2007 and 2012 that could explain either the absence of algae, or, any continued presence of acidity inconsistency".

Environmental monitoring and archived raw data from the past decade was analysed alongside the 2012 investigation to understand changes in geochemical, physical and biological ecosystems of the SSIX pit. This included analyses of climate data, geochemical analysis of water samples, phytoplankton counts, acidity titration curves and comparison of archived aerial imagery of the SSIX pit. This data was specifically compared alongside the scenarios and data collected from 2007 and 2012.

Statistical analysis of the 2007 data was unable to establish any significant correlations between rainfall and major ion concentrations and acidity. However, the temporal comparison between rainfall and major ion concentrations provided convincing trends, forming the foundations for conclusions in this project. The following section describes the principal conclusions from this project.

7.2 Principal Conclusions

7.2.1 Environmental Monitoring Geochemical Analyses

- Through the comparison of water sample geochemical analyses from the SSIX pit (collected by RTIO over the past decade), a convincing temporal trend can be found between seasons/periods of increased rainfall and increased concentrations of major ions in solution (largely dissolved metals). Equally, decreased concentrations of major ions are seen in the dry season/periods. This is considered to be due to the surface runoff of further oxidation products, from the MCS exposed on the pit wall, into the SSIX pit; adding to the production of AMD.
- Similar acidic surface runoff is produced in the SEP pit, where MCS is exposed on the pit walls. Acidity produced from the source water input is determined to also be a major influence on the water chemistry of the SSIX pit (from the SEP pit and related bores). This is determined by multiple Schoeller diagram comparisons between source water chemistry related to eventual SSIX pit water chemistry. An important example of this is seen in low concentrations of major ions in the 2007 total SEP discharge into the SSIX pit, which mirrored low concentrations of major ions in the SSIX pit water geochemistry.

7.2.2 Phytoplankton Presence

- Phytoplankton presence in the SSIX pit has been attributed to periods of low concentrations of major ions in solution (metal ions). This is attributed to metal phytotoxicity. This is equally observed when associated with low Cu concentrations, which appear to coincide with the re-appearance of phytoplankton.
- Phytoplankton presence has been determined to not solely be attributable to green colouration in the SSIX pit water. Occurrences of green water in the SSIX pit were apparent in 2012, when laboratory analysis confirmed absence of phytoplankton. With this discovery, 3 categories of pit water colour have been determined for use only as potential indicators of water quality.

1. **Brown**: algal growth absence due to high concentrations of metal precipitate in solution (e.g iron precipitate).
2. **Translucent green**: blue, green and white coloured metal ion precipitates (e.g. copper and aluminium sulphates and calcium anhydrite).
3. **Opaque green**: likely indication of algal presence, to be determined by laboratory phytoplankton count.

7.2.3 Acidity Inconsistency

- Acidity inconsistency (between total and calculated acidity) in the SSIX pit could not conclusively be attributed to organic acidity (produced by phytoplankton presence), due to the absence of phytoplankton (and any proof of organic acidity) in the 2012 investigation. However there is still potential that organic acidity is the key player in acidity inconsistency. This should be re-investigated in future work, when an algal growth is present.
  Literature provides evidence that acidity inconsistencies can occur from non-organic sources, such as the presence of alkalinity in a water sample, metal sequestration, or errors in lab methods and reporting.

7.3 Future work

RTIO is currently undertaking comprehensive environmental monitoring methods to obtain reliable geochemical analysis in regards to the mine water systems discussed in this thesis. Issues surrounding sampling temporal resolution are already being addressed by RTIO (Hannam et al., 2013), to increase to monthly sampling periods in the SSIX pit. This will acquire a more comprehensive data set for any future work to be completed on the geochemical characteristics of the SSIX pit.

It is recommended that further work regarding the acidity of the SSIX pit be conducted when a known algal growth is present. This will acquire more comparative data to the 2007 acidity inconsistency identified in the SSIX pit and further investigation into the potential of organic acids produced from algal growth.

RTIO should continue to use acidity titration curves as a method of analysis, or for occasional archive alongside SSIX pit lake geochemical data. The use of acidity titration curves remains an important tool when understanding the acidic species

present and their relative quantities and behaviour in a water sample. This is information that cannot be deduced from the total or calculated acidity values.

Previous sections in this thesis have suggested methods (such as the use of algacides or biocides) for removal of the algae identified in this project in order to resolve any further issues created by algal growth in the SSIX pit.

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Appendix I

Table A1 1. SGS laboratory geochemical analysis results for water source discharge to the SSIX pit in 2007 and 2012.

Location	Date	pH	TDS mg/L	TSS mg/L	COD mg/L	Alkalinity mg/L	Acidity mg/L	EC mg/L	Aluminium mg/L	Arsenic mg/L	Calcium mg/L
WB03SEP01	31/08/2007	5.04	500	<5	<5	8	230	-	0.53	<0.001	23
WB05SEP01	31/08/2007	5.52	220	<5	<5	20	210	-	<0.02	<0.001	9.7
WB05SEP02	31/08/2007	5.19	270	<5	<5	12	250	-	0.05	0.011	7
WB06SEP01	03/02/2012	2.5	1920	-	-	<5	5700	3200	98	0.003	45
WB06SEP01	22/08/2012	2.7	950	6	110	<5	310	1700	39	<0.10	34
WB11SEP02	03/02/2012	7.5	360	-	-	190	83	660	0.030	<0.001	44
WB11SEP02	22/08/2012	7.5	400	<5	230	220	5	720	<0.02	<0.020	39
SEP (DB3)	31/08/2007	4.17	760	<5	<5	<5	270	-	5.1	<0.001	26
Cyclone Tank	31/08/2007	-	460	<5	<5	7	220	-	1.9	0.003	17
Cyclone Tank	03/02/2012	3.1	796	-	-	<5	3400	1300	33	0.001	43
Cyclone Tank	13/04/2012	3.2	850	55	<10	<10	230	1200	0.05	<0.02	4.9
Cyclone Tank	05/07/2012	3.9	960	25	18	<5	190	1100	29	<0.10	36
SSIX Discharge	13/04/2012	2.5	1900	9	<10	<5	590	2600	0.03	<0.02	6.8
SSIX Discharge	05/07/2012	3.1	970	10	21	<5	<1	1500	39	<0.10	38
SEP Pit	03/02/2012	2.5	1790	-	-	<5	5700	3500	170	0.17	53
SEP Pit	22/08/2012	7.9	500	200	120	150	<5	740	0.04	<0.020	36

Table A1 2. SGS laboratory geochemical analysis results for water source discharge to the SSIX pit in 2007 and 2012.

Location	Date	pH	Sodium mg/L	Nickel mg/L	Zinc mg/L	Silica mg/L	Sulphate mg/L	Nitrate mg/L	Bicarbonate mg/L	Carbonate mg/L
WB05SEP03	31/08/2007	5.04	50	0.06	0.051	56	160	40	10	<1
WB05SEP01	31/08/2007	5.52	34	0.005	0.026	21	55	2.9	25	<1
WB05SEP02	31/08/2007	5.19	30	0.03	0.030	23	95	<0.2	15	<1
WB06SEP01	03/02/2012	2.5	42	1.0	0.59	47	1500	13	<5	<1
WB06SEP01	22/08/2012	2.7	47	0.41	0.28	54	610	6.0	<5	<1
WB11SEP02	03/02/2012	7.5	38	0.002	0.011	15	53	3.3	230	<1
WB11SEP02	22/08/2012	7.5	34	0.006	<0.01	17	45	3.9	270	<1
SEP (DB3)	31/08/2007	4.17	44	0.24	0.27	55	380	16	<5	<1
Cyclone Tank	31/08/2007	-	39	0.10	0.11	40	200	15	10	<1
Cyclone Tank	03/02/2012	3.1	39	0.33	0.34	25	570	6.2	<5	<1
Cyclone Tank	13/04/2012	3.2	160	0.006	0.04	-	490	6.2	<5	<1
Cyclone Tank	05/07/2012	3.9	40	0.41	0.44	43	590	4.1	<5	<1
SSIX Discharge	13/04/2012	2.5	180	0.008	0.04	-	1400	6.0	<5	<1
SSIX Discharge	05/07/2012	3.1	41	0.49	0.82	45	600	4.7	<5	<1
SEP Pit	03/02/2012	2.5	38	1.9	1.3	36	2600	8.2	<5	<1
SEP Pit	22/08/2012	7.9	43	0.26	0.24	37	110	3.2	180	<1

Table A1 3. SGS laboratory geochemical analysis results for water source discharge to the SSIX pit in 2007 and 2012.

Location	Date	pH	Chloride mg/L	Chromium mg/L	Copper mg/L	Iron mg/L	Mercury mg/L	Potassium mg/L	Magnesium mg/L	Manganese mg/L
WB03SEP01	31/08/2007	5.04	130	<0.005	0.027	<0.02	0.0009	10	38	0.82
WB05SEP01	31/08/2007	5.52	82	<0.005	0.008	0.22	0.0012	7.3	16	0.005
WB05SEP02	31/08/2007	5.19	84	<0.005	0.003	5.2	<0.0001	6.9	25	0.40
WB06SEP01	03/02/2012	2.5	98	0.096	1.5	110	<0.00005	6.5	68	4.8
WB06SEP01	22/08/2012	2.7	110	<0.025	0.44	4.7	0.00023	7.7	56	4.5
WB11SEP02	03/02/2012	7.5	84	<0.001	0.002	<0.02	<0.00005	7.6	36	0.21
WB11SEP02	22/08/2012	7.5	84	<0.005	<0.005	0.04	0.00005	6.6	33	0.21
SEP (DB3)	31/08/2007	4.17	81	<0.01	0.075	0.15	0.0001	12	76	3.5
Cyclone Tank	31/08/2007	-	91	<0.005	0.033	1.1	0.0004	9.5	44	1.5
Cyclone Tank	03/02/2012	3.1	89	0.018	0.58	6.0	<0.00005	7.6	46	1.7
Cyclone Tank	13/04/2012	3.2	91	<0.005	<0.005	<0.02	<0.00005	2.8	16	0.21
Cyclone Tank	05/07/2012	3.9	93	<0.025	0.32	12	<0.00005	8.6	63	4.6
SSIX Discharge	13/04/2012	2.5	90	<0.005	<0.005	0.30	<0.00005	3.2	19	0.38
SSIX Discharge	05/07/2012	3.1	95	<0.025	0.44	9.1	<0.00005	8.4	66	5.0
SEP Pit	03/02/2012	2.5	76	0.21	2.7	410	<0.00005	6.4	99	6.8
SEP Pit	22/08/2012	7.9	92	<0.005	0.014	0.25	0.00005	7.8	38	0.25

Table A1 4. SGS laboratory geochemical analysis results for water source discharge to the SSIX pit in 2007 and 2012.

Location	Date	pH	Cobalt mg/L	Phosphorous mg/L	TOC mg/L	BOD mg/L	Anion-Cation Balance
WB05SEP03	31/08/2007	5.04	0.04	<0.05	<1	<5	-
WB05SEP01	31/08/2007	5.52	<0.01	<0.05	<1	<5	-
WB05SEP02	31/08/2007	5.19	0.02	<0.05	<1	<5	-
WB06SEP01	03/02/2012	2.5	0.42	-	-	-	-38
WB06SEP01	22/08/2012	2.7	0.23	0.10	-	-	-
WB11SEP02	03/02/2012	7.5	<0.001	-	-	-	-1
WB11SEP02	22/08/2012	7.5	<0.01	0.02	-	-	-
SEP (DB3)	31/08/2007	4.17	0.18	<0.1	<1	<5	-
Cyclone Tank	31/08/2007	-	0.08	<0.05	<1	<1	-
Cyclone Tank	03/02/2012	3.1	0.15	-	-	-	-28
Cyclone Tank	13/04/2012	3.2	<0.01	-	-	-	-
Cyclone Tank	05/07/2012	3.9	0.26	-	-	-	-
SSIX Discharge	13/04/2012	2.5	<0.01	-	-	-	
SSIX Discharge	05/07/2012	3.1	0.29	-	-	-	-
SEP Pit	03/02/2012	2.5	0.81	-	-	-	-24
SEP Pit	22/08/2012	7.9	0.16	0.14	-	-	-

Appendix II

Table A2 1. SGS laboratory geochemical analysis results for the SSIX pit in 2007 and 2012 (* water chemistry data by Cawthron Labs, Nelson).

Location	Date	pH	TDS mg/L	TSS mg/L	COD mg/L	Alkalinity mg/L	Acidity mg/L	EC mg/L	Aluminium mg/L	Arsenic mg/L	Calcium mg/L
SSIX Pit	31/08/2007	3.58	560	14	9	<5	280	-	4.1	<0.001	22
SSIX Pit *	03/02/2012	3.3	720	-	<4	<1	200	120	25	<0.005	40
SSIX Pit	13/04/2012	2.6	2000	34	<10	<5	590	2500	82	<0.02	36
SSIX Pit	05/07/2012	3.1	1100	17	35	<5	300	1500	39	<0.10	39
SSIX Pit	22/08/2012	4.1	730	11	1000	<5	98	1000	14	<0.020	27
SSIX Pit	03/12/2012	3.5	730	13	11	<5	130	1100	17	<0.020	27

Table A2 2. SGS laboratory geochemical analysis results for the SSIX pit in 2007 and 2012 (* water chemistry data by Cawthron Labs, Nelson).

Location	Date	pH	Chloride mg/L	Chromium mg/L	Copper mg/L	Iron mg/L	Mercury mg/L	Potassium mg/L	Magnesium mg/L	Manganese mg/L
SSIX Pit	31/08/2007	3.58	99	<0.01	0.071	1.6	0.0002	11	53	2.2
SSIX Pit *	03/02/2012	3.3	82	0.0110	0.39	0.73	<0.0005	7.5	44	2.3
SSIX Pit	13/04/2012	2.6	88	0.081	1.2	130	<0.00005	7.1	61	3.7
SSIX Pit	05/07/2012	3.1	95	<0.025	0.44	10	<0.00005	8.5	68	5.1
SSIX Pit	22/08/2012	4.1	97	<0.005	0.15	0.67	<0.00005	7.6	48	2.9
SSIX Pit	03/12/2012	3.5	110	<0.005	0.17	3.1	0.00011	9.7	53	3.0

Table A2 3. SGS laboratory geochemical analysis results for the SSIX pit in 2007 and 2012 (* water chemistry data by Cawthron Labs, Nelson).

Location	Date	pH	Sodium mg/L	Nickel mg/L	Zinc mg/L	Silica mg/L	Sulphate mg/L	Nitrate mg/L	Bicarbonate mg/L	Carbonate mg/L
SSIX Pit	31/08/2007	3.58	47	0.16	0.16	46	260	18	<5	<1
SSIX Pit *	03/02/2012	3.3	38	0.25	0.14	28	430	1.8	1.0	<1
SSIX Pit	13/04/2012	2.6	36	0.72	0.56	-	1400	6.3	<5	<1
SSIX Pit	05/07/2012	3.1	41	0.49	0.44	45	750	4.7	<5	<1
SSIX Pit	22/08/2012	4.1	35	0.26	0.24	37	430	4.3	<5	<1
SSIX Pit	03/12/2012	3.5	45	0.27	0.24	40	410	4.1	<5	<1

Table A2 4. SGS laboratory geochemical analysis results for the SSIX pit in 2007 and 2012 (* water chemistry data by Cawthron Labs, Nelson).

Location	Date	pH	Cobalt mg/L	Phosphorous mg/L	TOC mg/L	BOD mg/L	Cation-Anion Balance
SSIX Pit	31/08/2007	3.58	0.11	<0.1	1.2	<5	<5
SSIX Pit *	03/02/2012	3.3	0.12	<0.002	1.2	-	0.96
SSIX Pit	13/04/2012	2.6	0.33	-	-	-	-
SSIX Pit	05/07/2012	3.1	0.29	-	-	-	-
SSIX Pit	22/08/2012	4.1	0.16	-	-	-	-
SSIX Pit	03/12/2012	3.5	0.16	0.01	<0.2	<5	-

Appendix III

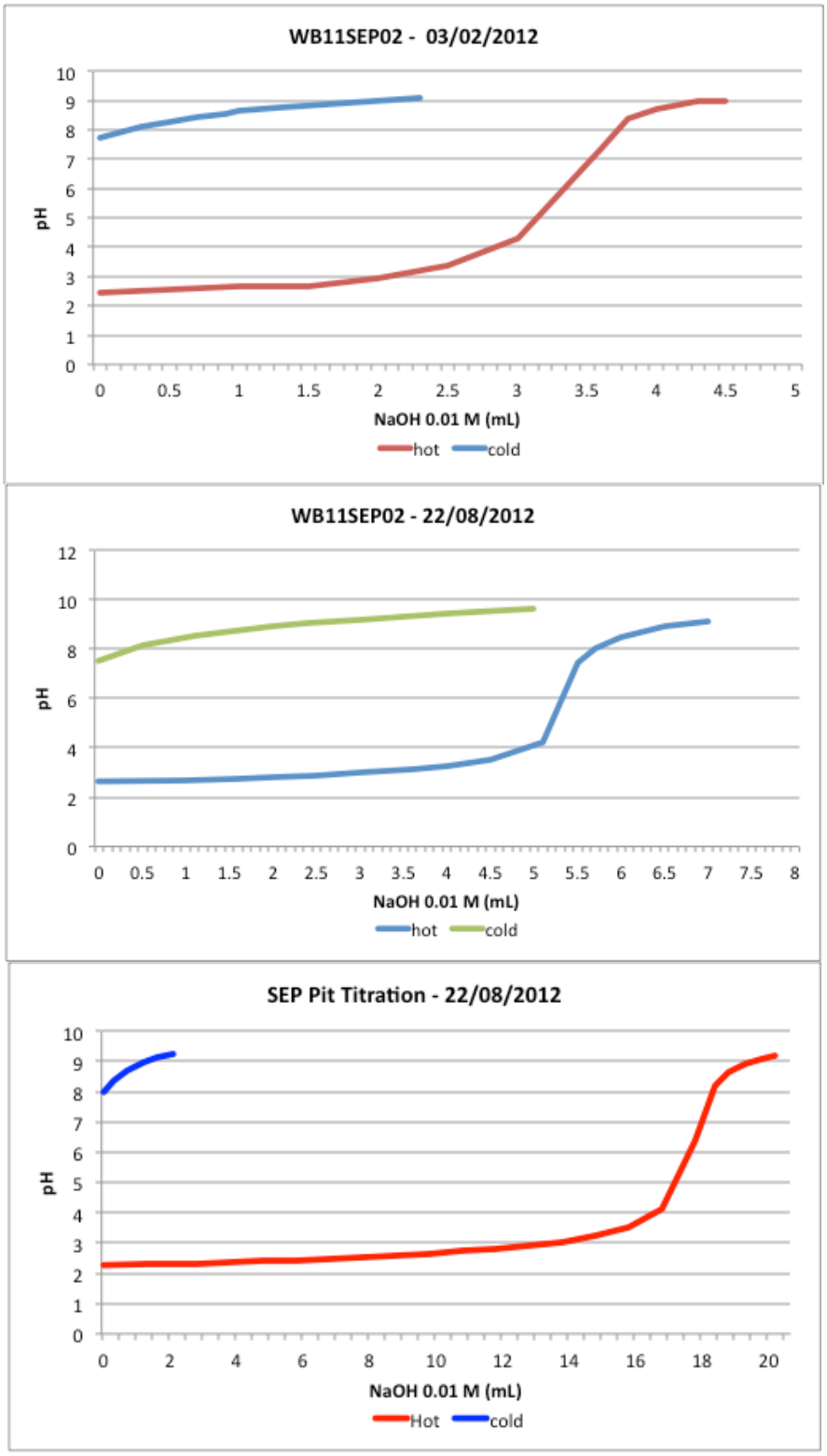

Figure A3 1. Comparison of hot and cold titration curves for the 2012 water samples with a neutral pH (see Table A3 1).

Table A3 1. Calculated and total (hot and cold acidity titration) acidity values for the 2012 water samples with a neutral pH. Showing acidity inconsistency due to presence of alkalinity.

	3/02/12	22/08/12	
	WB11SEP02	WB11SEP02	SEP Pit
Calculated Acidity			
Al (mg/L)	0.03	0.03	170
Fe (mg/L)	0	0	400
Mn (mg/L)	0.21	0.21	6.8
pH	7.5	7.5	7.9
Calculated Acidity as $CaCO_3$ (mg/L)	**0.55006599**	**0.550065987**	**2028.237282**
Total Acidity - Hot Titration			
NaOH used (mL)	3.8	5.5	18.4
NaOH normality (N)	0.01	0.01	0.01
H2S04 used (mL)	5	5	15
H2S04 normality (N)	0.02	0.02	0.02
HOT Total Acidity as $CaCO_3$ (mg/L)	**-124**	**-90**	**-232**
Total Acidity - Cold Titration			
NaOH used (mL)	0.5	0.5	0.3
NaOH normality (N)	0.01	0.01	0.01
H2S04 used (mL)	0	0	0
H2S04 normality (N)	0	0	0
COLD Total acidity as $CaCO_3$ (mg/L)	**10**	**10**	**6**
SGS actual acidity	**83**	**83**	**5700**

Appendix IV

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Project
MISC
Miscellaneous

Analyst ID
sabrina

DSID
2107

Report Date
11/09/2007

Batch Number
070904151201

Sample ID
13207 - 01

Date Collected
31/08/2007

Monitoring Point
13207 - 01

Sample Type
Phytoplankton

Date Received
3/09/2007

Functional Location ID
13207 - 01

Detection Limit
SRC LONG (44)

Analysis Date
6/09/2007

Units Reported Cell Density:cells mL^{-1} Biovolume: $mm^3 L^{-1}$ %: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Sample was clear and colourless. No algal colonies were visible.

Field Data Recording

Total Density
10,384.0 cells mL^{-1}

Total Counted
236

Uncertainty
13.0%

Species Name	Density	BioVolume	%
Chlorophyceae			
Chlamydomonas sp.	88		0.85
Chlamydomonas sp. 010	88		0.85
	176	**0.0000**	**1.69**
Cyanobacteria			
Synechocystis sp. 002	1,188	0.0097	11.44
Synechocystis sp. 003	9,020	0.0378	86.86
	10,208	**0.0475**	**98.31**

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 1. Original Dalcon Environmental report for phytoplankton count in the WB05SEP1 bore (August 2007).

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Analyst ID
sabrina

DSID
2109

Report Date
11/09/2007

Batch Number
070904151201

Sample ID
13207 - 03

Date Collected
31/08/2007

Monitoring Point
13207 - 03

Sample Type
Phytoplankton

Date Received
3/09/2007

Functional Location ID
13207 - 03

Detection Limit
SRC LONG (44)

Analysis Date
6/09/2007

Units Reported Cell Density:cells mL^{-1}

Biovolume: mm^3 L^{-1}

%: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Sample was clear and colourless. No algal colonies were visible.

Field Data Recording

Total Density
308.0 cells mL^{-1}

Total Counted
7

Uncertainty
75.6%

Species Name	Density	BioVolume	%
Chlorophyceae			
Chlamydomonas sp.	44		14.29
	44	**0.0000**	**14.29**
Cyanobacteria			
Synechocystis sp. 002	44	0.0004	14.29
Synechocystis sp. 003	220	0.0009	71.43
	264	**0.0013**	**85.71**

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Shading Key

Potentially toxic species

Potentially taste & odour causing species

Figure A4 2. Original Dalcon Environmental report for phytoplankton count in the WB05SEP2 bore (August 2007).

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Miscellaneous

Analyst ID
sabrina

DSID
2110

Report Date
11/09/2007

Batch Number
070904151201

Sample ID
13207 - 04

Date Collected
31/08/2007

Monitoring Point
13207 - 04

Sample Type
Phytoplankton

Date Received
3/09/2007

Functional Location ID
13207 - 04

Detection Limit
SRC LONG (44)

Analysis Date
6/09/2007

Units Reported Cell Density:cells mL^{-1} | Biovolume: mm^3 L^{-1} | %: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Sample was clear and colourless. No algal colonies were visible.

Field Data Recording

Total Density
3,652.0 cells mL^{-1}

Total Counted
83

Uncertainty
22.0%

Species Name	Density	BioVolume	%
Cyanobacteria			
Synechocystis sp. 003	3,652	0.0153	100.00
	3,652	**0.0153**	**100.00**

End Of Report

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 3. Original Dalcon Environmental report for phytoplankton count in the WB03SEP01 bore (August 2007).

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Miscellaneous

Analyst ID
sabrina

DSID
2111

Report Date
11/09/2007

Batch Number
070904151201

Sample ID
13207 - 05

Date Collected
31/08/2007

Monitoring Point
13207 - 05

Sample Type
Phytoplankton

Date Received
3/09/2007

Functional Location ID
13207 - 05

Detection Limit
SRC LONG (44)

Analysis Date
6/09/2007

Units Reported Cell Density:cells mL^{-1}

Biovolume: mm^3 L^{-1}

%: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Sample was clear and colourless. No algal colonies were visible.

Field Data Recording

Total Density
924.0 cells mL^{-1}

Total Counted
21

Uncertainty
43.6%

Species Name	Density	BioVolume	%
Cyanobacteria			
Synechocystis sp. 002	44	0.0004	4.76
Synechocystis sp. 003	880	0.0037	95.24
	924	**0.0041**	**100.00**

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 4. Original Dalcon Environmental report for phytoplankton count in the SEP Cyclone Tank (August 2007).

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Analyst ID
sabrina

DSID
2112

Report Date
11/09/2007

Batch Number
070904151201

Sample ID
13207 - 06

Date Collected
31/08/2007

Monitoring Point
13207 - 06

Sample Type
Phytoplankton

Date Received
3/09/2007

Functional Location ID
13207 - 06

Detection Limit
SRC LONG (44)

Analysis Date
6/09/2007

Units Reported Cell Density:cells mL^{-1}

Biovolume: $mm^3 L^{-1}$

%: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Sample was clear and pale green coloured. No algal colonies were visible.

Field Data Recording

Total Density
392,656.0 cells mL^{-1}

Total Counted
8,924

Uncertainty
2.1%

Species Name	Density	BioVolume	%
Chlorophyceae			
Chlorophyte 078	392,040		99.84
	392,040	**0.0000**	**99.84**
Cyanobacteria			
Synechocystis sp. 002	616	0.0050	0.16
	616	**0.0050**	**0.16**

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 5. Original Dalcon Environmental report for phytoplankton count in the SSIX pit (August 2007).

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Analyst ID
sabrina
Report Date
11/09/2007

DSID
2113

Batch Number
070904151201

Sample ID
13207 - 07

Date Collected
31/08/2007

Monitoring Point
13207 - 07

Sample Type
Phytoplankton

Date Received
3/09/2007

Functional Location ID
13207 - 07

Detection Limit
SRC LONG (44)

Analysis Date
6/09/2007

Units Reported Cell Density:cells mL^{-1} | Biovolume: $mm^3 L^{-1}$ | %: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Sample was clear and colourless. No algal colonies were visible.

Field Data Recording

Total Density
1,584.0 cells mL^{-1}

Total Counted
36

Uncertainty
33.3%

Species Name	Density	BioVolume	%
Chlorophyceae			
Chlorophyte 078	264		16.67
	264	**0.0000**	**16.67**
Cyanobacteria			
Synechocystis sp. 003	1,320	0.0055	83.33
	1,320	**0.0055**	**83.33**

End Of Report

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 6. Original Dalcon Environmental report for phytoplankton count in the SEP(DB3) bore (August 2007).

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DATA REPORT

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Project	Customer	Analyst ID	DSID
SSIX SSIX Pit Phytoplankton	Geological Sciences University of Canterbury Private Bag 4800 Christchurch New Zealand	Ling Admin **Report Date** 8/05/2012	17623

Batch Number 120420124756	**Sample ID** SEP Pit	**Date Collected** 19/04/2012
Monitoring Point Acid Mine Water	**Sample Type** Phytoplankton	**Date Received** 20/04/2012
Functional Location ID SEP Pit	**Method (Detection Limit)** Raw Count (1)	**Analysis Date** 8/05/2012

Units Reported Cell Density:cells mL^{-1} | Biovolume: mm^3 L^{-1} | %: Percentage of total cells counted

Sampler Notes

Laboratory Notes
A single cell that looked like a Chlamydomonas but without flagella was also observed.

Field Data Recording

Total Density	Total Counted	Uncertainty
280.0 cells mL^{-1}	280	12.0%

Species Name	Density	BioVolume	%
Unknown			
Unicellular coccoid alga sp. 001	280		100.00
	280	**0.0000**	**100.00**

End Of Report

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 7. Original Dalcon Environmental report for phytoplankton count in the SEP pit (April 2012).

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Project	Customer	Analyst ID	DSID
SSIX SSIX Pit Phytoplankton	Geological Sciences University of Canterbury Private Bag 4800 Christchurch New Zealand	Ling Admin **Report Date** 8/05/2012	17578

Batch Number	Sample ID	Date Collected
120416112957	SSIX Pit	13/04/2012
Monitoring Point	**Sample Type**	**Date Received**
SSIX Pit	Phytoplankton	16/04/2012
Functional Location ID	**Method (Detection Limit)**	**Analysis Date**
SSIX Pit	Raw Count (1)	8/05/2012

Units Reported Cell Density:cells mL^{-1} | Biovolume: mm^3 L^{-1} | %: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Algae and Cyanobacteria not detected.

Field Data Recording

Total Density	Total Counted	Uncertainty
0.0 cells mL^{-1}	0	

Species Name	Density	BioVolume	%
	0	0.0000	

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Shading Key
Potentially toxic species

Figure A4 8. Original Dalcon Environmental report for phytoplankton count in the SSIX pit (April 2012).

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Project	Customer	Analyst ID	DSID
SSIX SSIX Pit Phytoplankton	Geological Sciences University of Canterbury Private Bag 4800 Christchurch New Zealand	mitchell **Report Date** 17/10/2012	18470

Batch Number 120823084515	**Sample ID**	**Date Collected** 22/08/2012
Monitoring Point SSIX Pit	**Sample Type** Phytoplankton	**Date Received** 23/08/2012
Functional Location ID SSIX Pit	**Method (Detection Limit)** SRC CAMP (9)	**Analysis Date** 15/10/2012
Units Reported Cell Density:cells mL^{-1}	Biovolume: mm^3 L^{-1}	%: Percentage of total cells counted

Sampler Notes

Laboratory Notes
Algae and Cyanobacteria not detected.

Field Data Recording

Total Density	Total Counted	Uncertainty
0.0 cells mL^{-1}	0	

Species Name	Density	BioVolume	%
	0	0.0000	

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Shading Key
Potentially toxic species

Figure A4 9. Original Dalcon Environmental report for phytoplankton count in the SSSIX pit (August 2012).

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Project	Customer	Analyst ID	DSID
SSIX SSIX Pit Phytoplankton	Geological Sciences University of Canterbury Private Bag 4800 Christchurch New Zealand	mitchell **Report Date** 17/10/2012	18471

Batch Number 120823084515	**Sample ID**	**Date Collected** 22/08/2012
Monitoring Point Acid Mine Water	**Sample Type** Phytoplankton	**Date Received** 23/08/2012
Functional Location ID SEP Pit	**Method (Detection Limit)** SRC CAMP (9)	**Analysis Date** 15/10/2012
Units Reported Cell Density:cells mL^{-1}	Biovolume: mm^3 L^{-1}	%: Percentage of total cells counted

Sampler Notes

Laboratory Notes

Field Data Recording

Total Density	Total Counted	Uncertainty
99.0 cells mL^{-1}	11	60.3%

Species Name	Density	BioVolume	%
Bacillariophyceae			
Nitzschia spp.	45		45.45
	45	**0.0000**	**45.45**
Unknown			
Unicellular coccoid alga sp. 001	54		54.55
	54	**0.0000**	**54.55**

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 10. Original Dalcon Environmental report for phytoplankton count in the SEP pit (August 2012).

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Project	Customer	Analyst ID	DSID
SSIX SSIX Pit Phytoplankton	Geological Sciences University of Canterbury Private Bag 4800 Christchurch New Zealand	sabrina **Report Date** 6/02/2013	19271

Batch Number	Sample ID	Date Collected
121205084331	SSIX Pit	3/12/2012
Monitoring Point	**Sample Type**	**Date Received**
SSIX Pit	Phytoplankton	4/12/2012
Functional Location ID	**Method (Detection Limit)**	**Analysis Date**
SSIX Pit	Qualitative Count (1)	6/02/2013

Sampler Notes

Field Data Recording

Laboratory Notes

Raw sample was concentrated 10x which resulted in a lot of non algal particulate matter, during quantitative analysis no algal cells were detected.
A live sample analysis was undertaken using fluorescence resulting in a few cells of Synechococcus sp. and an unidentifiable cyanobacterial filament being recorded.

Total Density	Total Counted	Uncertainty

Species Name	Notes
Cyanobacteria	
Cyanobacteria filaments	Present
Synechococcus sp.	Present

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Shading Key
Potentially toxic species
Potentially taste & odour causing species

Figure A4 11. Original Dalcon Environmental report for phytoplankton count in the SSIX pit. The unaccountable status 'Present' determines an insignificant phytoplankton count (December 2012).